Hierarchical Thermodynamic Metrics for Evaluating the Environmental Sustainability of Industrial Processes

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Industrial progress toward sustainability requires meaningful, practical, and scientifically sound metrics. Most existing metrics rely on information about material and energy inputs and emissions from the main process and selected processes in its life cycle. Such metrics often result in multiple conflicting variables, making it difficult to use them for decision making. Furthermore, sustainability metrics need to be scientifically rigorous and capable of evaluating the broader economy and ecosystem scale impacts of selected processes and products. This paper proposes a framework for evaluating the environmental sustainability of industrial processes that satisfies these needs. This framework uses exergy analysis to combine different types of material and energy streams in a thermodynamically sound manner. Exergy analysis is also combined with end-point life-cycle impact assessment methods for evaluating the impact of emissions. This results in metrics for a selected system with different levels of aggregation ranging from multiple to single dimensions. The challenge of analyzing a process at life cycle and coarser spatial scales is met by combining exergy analysis, life cycle assessment, input–output analysis, and both economic and ecological aspects. The result is a doubly nested hierarchy, which analyzes processes at multiple spatial scales of process, life cycle, economy, and ecosystem. Each scale contains another hierarchy based on the degree of aggregation of the metrics. A case study of the ammonia process illustrates the characteristics of the proposed approach. © 2004 American Institute of Chemical Engineers Environ Prog, 23: 302–314, 2004

1. INTRODUCTION

Businesses are continuing to realize the strategic importance of improving the sustainability of their activities due to its contribution to improving both, tangible and intangible assets [1, 2]. However, realizing these benefits requires appropriate tools and techniques for evaluating processes and to guide selection toward the best alternative. Industrial sustainability metrics aim to quantify the ecological, economic, and social aspects of processing systems and their life cycles to facilitate sound decision making. The challenges in developing such metrics for industrial processes and the variety of existing approaches are described in recent papers [3–5]. Popular approaches relevant to chemical processes include those developed by the American Institute of Chemical Engineers in the United States [6, 7] and by the Institution of Chemical Engineers in the United Kingdom [8]. Similar efforts are also being made by industry groups such as the Global Reporting Initiative (www.globalreporting.org) and the World Business Council for Sustainable Development (www.wbcsd.org). Because of these efforts, a variety of practical and industrially relevant metrics have already been developed and applied to quantify the sustainability of economic and industrial activities [9]. These metrics typically include measures of pollutant output, process performance, and direct and indirect effects of an activity on the environment and society.

In general, these approaches categorize the environ-

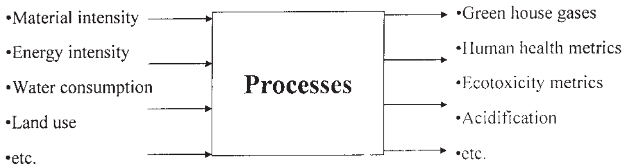

Figure 1. Sustainability metrics of AIChE–CWRT (Schwarz et al., 2002).

mental effects of industrial processes into input side and output side metrics, as shown in Figure 1. Basic environmental sustainability metrics include material intensity, energy intensity, water consumption, toxic emission, pollutant emission, and carbon dioxide emission. These input and output variables are normalized by measures such as mass of product, dollars of value added, or dollars of revenue. Additional metrics for specific types of impact of pollutants, land use, and social aspects may also be developed. The desirable characteristics for industrial sustainability metrics include: simple to calculate, useful for decision making, understandable to different audiences, cost-effective, robust and nonperverse in indicating progress toward sustainability, stackable to permit combination with metrics for other processes, and protective of proprietary information [7]. The calculations for these metrics are relatively straightforward, and have been carried out for a large number of chemical processes by Schwarz *et al.* [7].

However, some of the shortcomings faced by such approaches for practical metrics include the following.

- *Curse of dimensionality.* A large number of, often conflicting, metrics and variables make the decision-making task quite challenging.
- *Perverse results arising from lack of theoretical rigor.* Adding the mass or energy of different streams to compute the material or energy intensity focuses only on the first law of thermodynamics and ignores the second law. This can lead to perverse results such as improvement in metrics by switching to a higher quality but scarce energy source. Furthermore, mass and energy usually cannot be separated for any stream, and the separate consideration of both streams may introduce redundancy and double counting.
- *Challenge of multiple scales.* A rigorous and comprehensive method for considering inputs and impacts of the selected process at multiple spatial scales is crucial. Otherwise, use of a narrow spatial boundary may improve sustainability by simply shifting the impacts outside the boundary.

This paper proposes the use of thermodynamic methods at multiple spatial scales to overcome these shortcomings while retaining the attractive characteristics of practical sustainability metrics. The use of thermodynamic methods for evaluating sustainability of industrial products and processes is motivated by the fact that all activities on earth rely on the availability of energy and its conversion to various goods and services. Ultimately, all planetary activities depend on exergy or available energy [10–14], making it the ultimate limiting resource. Exergy provides a scientifically rigorous way to compare and combine streams of material and energy, and represents environmental impact and information content. It has been most popular for analyzing chemical and thermal processes to improve their efficiency [12]. An influential report by Ford *et al.* [15] demonstrated the benefits of exergy analysis for improving energy efficiency. Unlike energy or mass, exergy is able to jointly represent material and energy streams. Ayres *et al.* [16] also suggested that the exergy of emissions could provide a proxy for the potential impact of the emissions. Such an approach is useful for quick and approximate evaluation of environmental impact without a detailed impact analysis. The limited validity of this connection between exergy of emissions and their impact is demonstrated by Dincer [17] and Seager and Theis [18].

These ideas have also been incorporated into environmental sustainability metrics. For example, Berthiaume *et al.* [19] proposed a renewability indicator of a biofuel based on the net exergy produced in a process and the exergy required for reducing the impact of emissions by converting them into a benign state. The difference between these two exergy values is the useful work, and the renewability indicator is calculated as a ratio of the useful work to the produced work. Such an approach is difficult to use without detailed knowledge about the process life cycle. Dewulf *et al.* [20] quantified sustainability using renewability and efficiency parameters. The renewability parameter is the ratio of the exergy consumption of renewable resources to the total exergy consumption. The efficiency parameter is the ratio of the exergy value of the useful products to the sum of exergy consumed in the process and that required for abatement of harmful emissions. Lems *et al.* [21] used the depletion time of a resource, exergy efficiency of process, and exergy consumption for abatement of emission. The depletion time of a resource is used as a sustainability index because it can represent both renewable and nonrenewable resource in a consistent manner. The depletion time is converted into an abundance factor to have a scale of zero to one. This approach faces challenges in determining the relevant parameters for each resource, and ignores the effect of market forces on the depletion time.

The approach proposed in this paper enhances the metrics described in Schwarz *et al.* [7]. Exergy is used for reducing dimensionality on the input side of Figure 1 by combining material and energy streams in a theoretically rigorous manner. This combination is possible because the utility of any material or energy stream is in its ability to do work, and exergy represents this useful part of any material or energy stream. It is quantified as the thermodynamic distance or distinguishability from the reference environment. On the output side, the dimensionality may be reduced in two ways. The exergy of all the output streams can be calculated, as for the inputs, and may roughly correspond to the impact of the outputs on the environment [16, 18]. Unfortunately, the relationship between the exergy of emissions and their impact is often tenuous. Consequently, if end-point impact assessment methods are available [22], then the impact of emissions may be represented in terms of exergy loss of the impacted system, or its ability to do useful work. Finally, the input and output side results may be combined to yield a single aggregate metric. This aggregation may be done in a few different ways depending on the normalization. This approach results in a hierarchy of metrics at different levels of aggregation, and uses a scientifically sound approach for addressing the first two shortcomings listed above. Existing data on sustainability metrics used in Schwarz *et al.* [7] and related work for individual processes may be readily used for developing this hierarchy at the *process scale*. The challenge of multiple spatial scales is addressed by including information about the life cycle, other economic sectors, and contribution of ecological goods and services. Expansion to the life-cycle scale is accomplished by using information about selected processes in the life cycle, as suggested by ISO 14000 [23], whereas information about economic sectors and ecosystems is incorporated by input–output analysis [21, 25]. The result is a doubly nested hierarchy, which consists of multiple spatial scales and different levels of aggregation for the nodes at each scale. These scales are selected to capture the global nature of sustainability, along with the need of connecting it to local decisions at smaller scales. The selected scales of equipment, life cycle, economy, and ecosystem correspond with type of data and models that are currently available.

This paper demonstrates the features and benefits of exergy analysis and multiscale hierarchical metrics. It does not focus on decision making or evaluating specific metrics, but other exergy metrics such as those described earlier may be readily calculated from the results of the proposed approach. The hierarchical structure permits gradual expansion of the scale of analysis from the equipment to the economy scales. This approach is illustrated by application to an ammonia process and its coarser spatial scales.

The rest of the paper is organized as follows. The use of exergy analysis is explained to evaluate the resource consumption and emission impacts in section 2. Hierarchical metrics for process scale and life-cycle scale are discussed using industrial and ecological cumulative exergies in section 3. Case studies are implemented for an ammonia process in section 4 followed by discussion and conclusions in section 5.

2. EXERGY ANALYSIS FOR ENVIRONMENTAL SUSTAINABILITY

This section introduces the basic principles of exergy analysis and its extensions for environmentally conscious decision making. Brief descriptions are provided about the approaches relevant for calculating input and output side metrics followed by simple illustrations of the benefits of a thermodynamic approach for evaluating the sustainability of industrial processes.

2.1. Exergy Analysis

Exergy is defined as the maximum amount of work that can be produced by a stream of matter, heat, or work as it equilibrates with a reference environment [12]. It is commonly be represented per unit mass as

$$B = \Delta\left[H - T_0 S + \sum_i x_i \mu_i + v^2/2 + gz \right] \tag{1}$$

where H is enthalpy, S is entropy, x_i is the mole fraction of component i, μ_i is the chemical exergy of component i, v is velocity, and z is height. T_0 is temperature of the reference environment, and Δ means the difference with respect to the temperature, pressure, and composition between the current state and the reference environment represented by the subscript 0. The first two terms represent physical exergy, the third term chemical exergy, the fourth term kinetic exergy, and the last term potential exergy. In typical industrial processes, the kinetic and potential exergies are negligible and only physical and chemical exergies are evaluated, which together constitute thermal exergy [12]. Exergy is a state variable, and its value depends on the reference state. For environmental applications, the reference is usually selected as the average for the natural environment [12]. Exergy is not subject to a conservation law, and is consumed or destroyed in irreversible processes. Therefore, exergy has been successfully applied to evaluate the thermodynamic efficiency and reduce energy consumption of chemical and thermal processes [26].

2.2. Industrial and Ecological Cumulative Exergy Consumption

Cumulative exergy consumption (CEC) is very relevant to evaluating environmental sustainability because it expands exergy analysis to a larger spatial scale by considering a partial life cycle. Traditional or Industrial CEC (ICEC) is the total exergy consumption in all industrial processes in the supply chain of a product up to the resources extracted from nature [12]. ICEC treats all inputs from ecosystems to be thermodynamically equivalent by ignoring the exergy required for the creation of ecosystem goods and services. Because the exergy consumption in ecosystems is quite large, and the resulting resources provide the crucial foundation for all economic activity, accounting for the contribution of ecosystems is important, particularly for gaining insight into environmental sustainability. Ecological CEC (ECEC) includes such information along with ICEC to account for the contribution of ecosystems [27]. This concept is closely related to the concept of emergy developed in systems ecology [11].

In this paper, both ICEC and ECEC are calculated for the proposed hierarchy of sustainability metrics. These CECs are calculated for selected processes using traditional exergy analysis combined with knowledge about the thermodynamic efficiency of creating various inputs from ecosystems. ICEC and ECEC values at the economy scale are calculated by a thermodynamic input–output model developed for the U.S. economy [25]. This model provides ratios of the throughput of ICEC to money and ECEC to money for each economic sector. These ratios are used along with the cost of economic inputs to the selected process or life cycle to estimate the exergy consumption at the economy and ecosystem scales, as demonstrated in section 4. The result is a hybrid approach that combines information at the process, life cycle, economy, and ecosystem scales.

2.3. Exergy of Material and Energy Streams

Exergy can be calculated for all kinds of material streams using Eq. 1, and that of energy streams by multiplying the heat content with the Carnot efficiency, while work is equal to exergy [12, 28]. Such calculations require knowledge about the physical and chemical states of each stream and a selected reference state, and permit scientifically sound reduction in dimensionality, which makes it possible to combine all material and energy streams into one exergy quantity. Standard chemical exergies for a variety of material and energy carrier streams have also been calculated by Szargut *et al.* [12]. The environmental reference state that is commonly used is at 1 atm, 25° C, and composition of the air, oceans, and a selected thickness of the earth's crust. Additional details about exergy calculations including tables of standard chemical exergy values for common chemicals are available in the literature [12, 28].

2.4. Exergy of Output Streams and Their Impact

As mentioned in section 1, this paper considers two approaches for combining the exergy of process outputs: direct addition of the exergy of the output streams, or assessing the impact of emissions and representing it as a loss of exergy of the impacted system. Both approaches are described in brief in this section.

Exergy of useful products is commonly used for calculating thermodynamic efficiency. In addition, exergy of waste products has been suggested as a way of quantifying the impact of emissions. Several researchers have hypothesized that, because exergy of emissions represents their ability to do work on the environment, it may be related to their impact. A recent study by Seager and Theis [18] used the exergy of mixing to quantify environmental impact of air pollutants.

$$B_{mix} = nRT_0 \ln\left(\frac{y}{y^0}\right) \qquad (2)$$

where B_{mix} is the exergy change of a substance when its activity changes from y^0 to y, n is the total number of moles, y is the activity in the thermodynamic system under consideration, and y^0 is the reference activity in the environmental sink. However, the computation results for exergy of mixing are very sensitive to the choice of reference state, and chemical species that do not exist at all in nature would have an infinite exergy of mixing. Seager and Theis [18] have found only a limited relationship between the exergy of emissions and their environmental impacts. However, this measure may provide an approximate estimate and may be useful if detailed impact analysis is not available.

Impact assessment by "end-point" methods considers the likely effect of emissions on human and ecological systems [22]. If such analysis is available, then the results from end-point methods can be converted into exergetic terms [25, 29]. For example, an end-point impact assessment method such as, Eco-indicator 99 measures human health impact in terms of disability-adjusted life years (DALY). DALY represents the total years of healthy life lost as a result of premature mortality or some degree of disability caused by the emission. The results of Eco-indicator 99 may be converted into thermodynamic terms since impact may be viewed as a loss of human or ecosystem ability to do work. For converting DALY of substance i ($DALY_i$) to exergy loss resulting from human health impact ($B_{impact,i}$), it must be multiplied with its mass flow m_i, and a conversion factor, representing the exergy consumption of the population concerned.

$$B_{impact,i} = m_i \cdot DALY_i \cdot \xi_i \qquad (3)$$

The conversion factor ξi may be calculated as a product of the exergy consumed by an average person and the ratio of the average payroll of the affected population to the mean average payroll. This ratio assumes that human exergy is proportional to their skill level, as quantified by their payroll.

2.5. Illustrations of the Benefits of Thermodynamic Metrics

The following simple illustrations show how sustainability metrics based on material or energy intensity can lead to perverse results and how exergy-based metrics may be able to overcome this shortcoming.

Energy vs. Exergy Metrics for Hot Water

Consider two sources of hot water, Stream 1 at 75° C and flow rate of 20 kg/h, and Stream 2 at 45° C and flow rate of 50 kg/h. The enthalpy content of both streams is equal, implying that energy metrics for both streams would also be equal. The fact that the hotter stream is much more useful, because of its ability to heat a wider range of temperatures, is not captured by energy metrics. However, the exergy content of both streams is very different, and is able to capture the difference in the quality of both streams. Stream 1 has an exergy of 75.6 kcal/h vs. 32.1 kcal/h for Stream 2. Thus, in this case, exergy metrics provide much more meaningful information. In fact, the ratio of exergy to enthalpy has been suggested as a measure of quality [30]). If material and energy metrics are used together, then the smaller material intensity of Stream 1 indicates the higher quality of this stream. However, this approach requires consideration of two dimensions (material and energy) and ignores the second law, whereas exergy is more rigorous because of consideration of the first and second laws with only one dimension.

Maleic Anhydride Processes

Input-side metrics are calculated for two alternative processes for making maleic anhydride [31]. Both processes consume *n*-butane and oxygen as raw materials, but in different amounts. Table 1 shows material and exergy intensities of the two processes per pound of maleic anhydride produced. The material intensity of Process A is larger than that of Process B, which implies that Process B may be preferable from the perspective of resource consumption. Exergy analysis of both processes leads to the opposite conclusion because this approach accounts for the fact that oxygen is a lower quality material source than butane. That is, butane is

Table 1. Comparison of material intensity and exergy for two maleic anhydride processes.

Intensity	Process A	Process B
Material (lb/lb product)		
Butane	0.073	0.316
Oxygen	5.745	2.176
Total	5.818	2.492
Exergy (Btu/lb product)		
Butane	2.236×10^4	2.742×10^4
Oxygen	2.079×10^{-1}	9.798×10^{-2}
Total	2.236×10^4	2.742×10^4

farther away from the ambient environment than oxygen, or oxygen is more plentiful than butane. Using less butane and more oxygen is better for the conservation of resources. Thus, exergy-based metrics guide toward the conservation of limited resources because chemical exergy calculated with an environmental reference state can roughly correspond to the scarcity of natural resources [32].

Thermodynamic Metrics for Processes

The first example above illustrates how exergy per unit enthalpy is a metric of energy quality of a material. The corresponding metric for evaluating processes is suggested to be the ratio of exergy to the ICEC for the process supply chain [12]. This ratio, called industrial cumulative degree of perfection (ICDP), ignores the contribution of ecosystem goods and services or natural capital, and may result in misleading metrics. As illustrated by Hau and Bakshi [27], the ICDP of coal-based electricity is higher than that of solar thermal electricity. This is a potentially misleading result from the viewpoint of sustainability, given that coal is a finite resource, unlike sunlight. This approach ignores the fact that coal is a much higher quality and scarce energy source than sunlight. In contrast, the ecological CDP (ECDP), calculated by including the ecosystem goods and services required for making natural resources, provides the opposite result. This is because emergy or ECEC is a better indicator of the scarcity of natural resources, given that greater reliance on ecological goods and services usually implies less availability of the resource [11]. More research is required to evaluate the benefits of ECEC for sustainability analysis and metrics.

3. HIERARCHICAL METRICS

Because of the complex and multidimensional nature of sustainability, a hierarchy of metrics is convenient for combining results from different studies [7], capturing the multiscale nature of sustainability [33], and allowing easier evaluation among alternatives [5]. Analysis of individual industrial processes is not enough for evaluating their sustainability because such a narrow view may simply shift the impacts to other parts of the life cycle. Consequently, sustainability metrics must be capable of linking small scales, such as an individual equipment or process with life-cycle scales, and extend further to scales of the economy and ecosystems [34]. Methods for including the life cycle are widely used and standardized by ISO 14000. Combining this Process LCA with Economic Input–Output LCA (EIO-LCA) is the focus of Hybrid LCA methods [35]. Another desirable property of sustainability metrics is that they must be stackable. Metrics for multiple systems or coarser scales should be obtainable by direct combination of individual metrics of constituent systems. This section describes a doubly nested hierarchy of metrics at multiple spatial scales, with another hierarchy based on the degree of aggregation at each scale. The spatial hierarchy represents the equipment, life cycle, economy, and ecosystem scales, whereas the aggregation hierarchy uses exergy to reduce dimensionality by combining material and energy flows.

3.1. Multiscale System

Figure 2 shows the conceptual diagram of flows for industrial and ecological processes [11, 36]. Industrial processes consume nonrenewable resources N, renewable ecosystem services and products R_1, and input from economy F. Economic inputs represent the things that are valued by the economy, and involve a monetary transaction. The outputs of industrial processes include the main products that are sold in the market Y, and emissions that are returned to the environment W. The ecosystem output R_2 represents nature's services needed to dissipate the emissions, and absorb their impact, respectively. This paper considers only the human impact of emissions.

The box representing industrial processes in Figure 2a may include a single process or a network of processes depending on the scale of analysis. At the process scale, only individual processes are considered, as depicted in Figure 2b. Information from selected multiple processes is combined to form the life-cycle scale. The economy scale also includes economic sectors represented by the box of "economic resources" in Figure 2a. Finally, the ecosystem scale includes ecological processes that lie outside the market.

3.2. Aggregation Hierarchy

The hierarchy representing different levels of aggregation or dimensionality reduction is depicted in Figure 3 for a selected system. Such a hierarchy may be readily developed at any spatial scale. At the base level (Level 1a), the left and right halves contain data about the inputs and outputs, respectively. These data may be in a variety of units such as mass, energy, or money. At Level 1b, all the data are converted into consistent thermodynamic units. This requires the use of methods described in section 2. It includes chemical and physical exergies because raw materials usually react to form products. At this level, details about all input and output streams are available without any aggregation resulting in a high dimensional space. Properties of the products, such as cost or exergy, may be incorporated in the metrics by normalization.

At the next level of the hierarchy (Level 2), the multitude of inputs and outputs are combined to yield more aggregate but separate metrics for the inputs and the impact of emissions. The impacts may be approx-

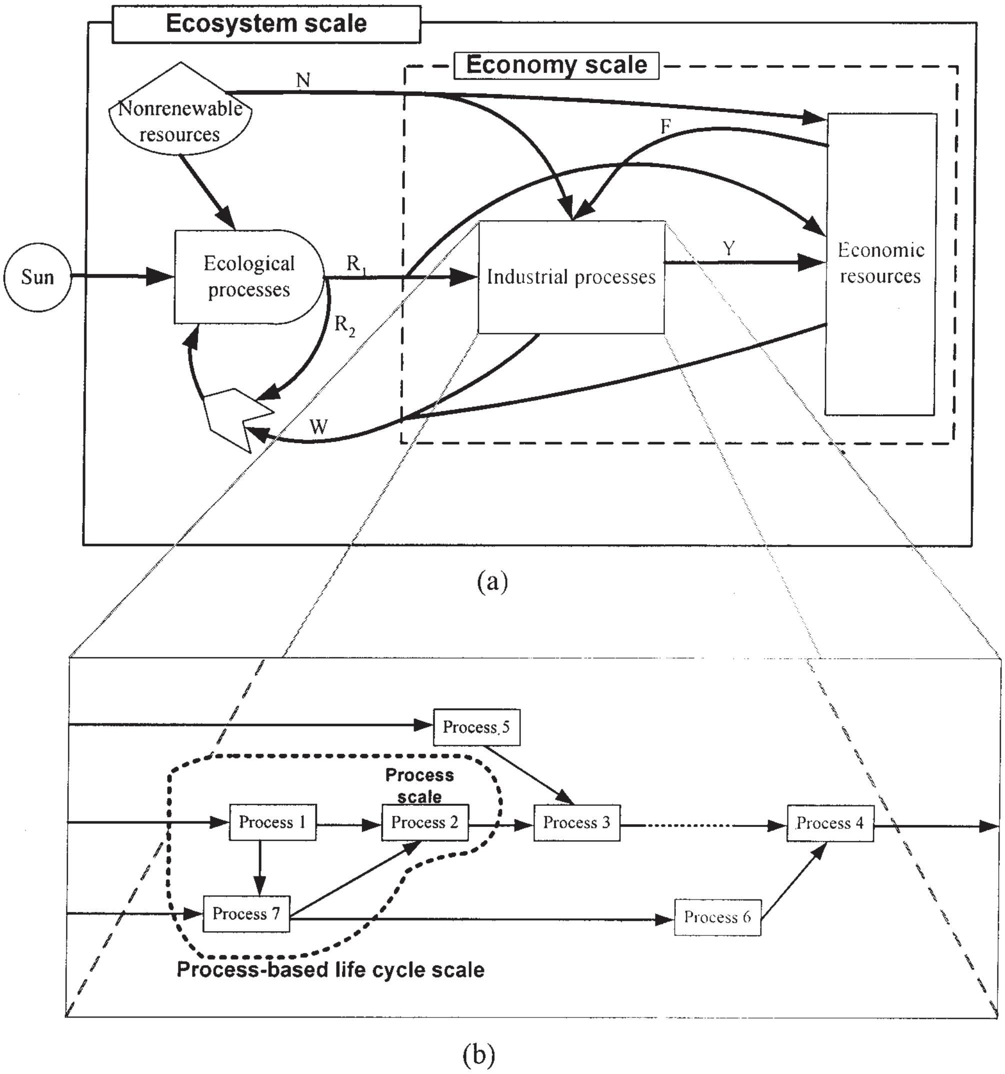

Figure 2. Energy flow diagram at multiple spatial scales. (a) Flow diagram for economy and ecosystem scales; (b) industrial processes considered for process and life-cycle scales.

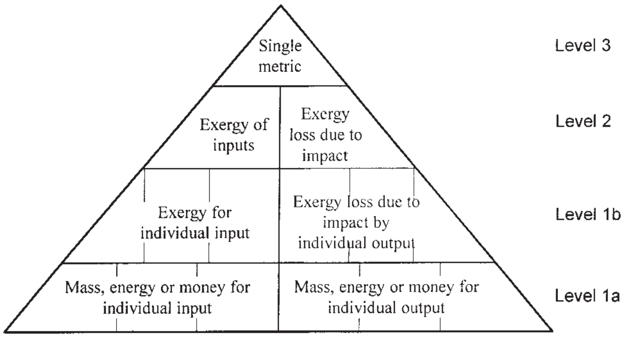

Figure 3. Hierarchical structure of sustainability metrics for a selected system.

imated by the exergy of the waste streams, or if endpoint impact assessment is available, by the exergy loss of human and ecological systems. The examples in this paper use the latter approach but consider only human impact. This aggregation can be done in a few different ways. Exergy of outputs may be classified as products (Y) and waste (W), and of inputs may be classified as direct renewable (R_1), direct nonrenewable (N), and direct economic (F). The impact of emissions represents the exergy required for dissipation of the emissions and the loss of exergy resulting from the ecological and human impact caused by the emissions.

At Level 3, a single metric may be obtained to represent the environmental sustainability of the selected system. Many different types of metrics may be defined by combining the variables at Level 2. The simplest and potentially most useful among these is the thermodynamic efficiency (or its reciprocal), which may be defined with or without including the impact of emissions. Alternatively, the economic value added or exergy of useful products may be used for normalization. In this work, the exergy values of input streams and the exergy loss resulting from the impacts of emissions are aggregated to obtain the single metric at Level 3. This represents the exergy change of the environment attributed to the consumption of raw material and the release of pollutants from the system at the selected scale. The proposed hierarchical structure eases the curse of dimensionality by aggregating multiple variables in a scientifically sound manner, while ensuring that details are still available. This approach allows the user to select the level of aggregation that is most useful for making decisions.

3.3. Spatial Hierarchy

Sustainable development cannot be accomplished by considering only a single spatial scale, and techniques and data are required for expanding the system boundary of a process or equipment to the entire life cycle, economy or ecosystem [34]. Conversely, if data and metrics are available at a coarse scale, they need to be translated to finer scales to permit detailed engineering decision making. The aggregation hierarchy presented in section 3.2 focuses on a system at a single scale. Similar hierarchies of metrics may be developed at other scales, and may be connected with each other to result in a spatial hierarchy, as described in this section.

Information for developing the aggregation hierarchy at the *process scale* may be readily obtained from mass and energy balances and cost information about the process from simulation or literature sources. Gate-to-gate inventory modules developed for specific processes may also provide useful information [37]. Such information also forms the basis of the metrics developed by AIChE–CWRT and others. Developing the aggregation hierarchy for the process scale would permit a conventional thermodynamic analysis, and inclusion of the impact of emissions allows consideration of some broader life-cycle aspects.

Expanding the analysis to the *life-cycle scale* involves selection of the most important processes in the life cycle. This approach is analogous to that used for process LCA, and may use the extensive life-cycle inventory databases included in various software packages. Converting the results of a process LCA into thermodynamic terms is quite straightforward if information about the physical and chemical properties of various streams is available. Data about cumulative exergy consumption (CEC) and cumulative degree for perfection (CDP) have been calculated for many common industrial processes, and may be used to calculate the life-cycle exergy consumption of selected products [12, 28]. Analysis at this scale ignores a large number of processes in the life cycle network, which together may introduce a significant error in the results.

The coarser *economy scale* considers activities in the entire economy to satisfy the requirements of the processes selected in the life cycle scale. This analysis relies on combining economic input–output LCA (EIO-LCA) with process LCA, resulting in an approach analogous to a tiered hybrid LCA [35]. EIO-LCA is applied to the streams that enter the process LCA based on their economic value, resulting in the material, energy, and emissions information arising from the economic inputs considered at the life-cycle scale. These may be converted into exergy values for Level 1b and Level 2 by the approaches described in section 2. The same result may also be obtained more conveniently by using the ratios of ICEC to money for economic sectors derived by the thermodynamic input–output analysis approach of Ukidwe and Bakshi [25]. This ratio indicates how much cumulative exergy is consumed in the entire economy per unit of monetary throughput in each industrial sector. Thus, the ICEC of each economic input may be calculated as

$$ICEC_i = m_i \cdot C_i \cdot R_{ICEC,i} \tag{4}$$

where $ICEC_i$ is the industrial cumulative exergy for product i, m_i is the mass flow of product i, C_i is the price of product per unit of mass, and $R_{ICEC,i}$ is the ratio of ICEC to money in the economic sector corresponding to product *i*. This analysis ignores the contribution of ecological goods and services for making various natural resources, which is equivalent to assuming that all natural resources require similar ecological effort. This assumption is clearly incorrect because coal and oil require much more input from nature than sunlight. The shortcomings of this assumption are discussed and illustrated in the last example of section 2.5 and by Odum [11] and Hau and Bakshi [27]. The ecosystem scale overcomes this shortcoming.

The *ecosystem scale* expands the analysis boundary to also account for the contribution of ecological goods and services. These inputs of natural capital form the basis of all economic activity, and ignoring them may result in transferring impacts to erosion of natural capital [38]. Determining the ecological cumulative exergy consumption throughout the life cycle for resources and impact of emissions is facilitated by the ratios of ECEC to money [25]. ECEC of each economic input is calculated by the following equation:

$$ECEC_i = m_i \cdot C_i \cdot R_{ECEC,i} \tag{5}$$

where $ECEC_i$ is the ecologically cumulative exergy for product i, m_i is the mass flow of product i, C_i is the price of product per unit of mass, and $R_{ECEC,i}$ is the ratio of ECEC to money in the economic sector corresponding to product *i*. This ratio provides information about how much exergy is consumed from the generation of natural resources to the generation of products per unit of monetary throughput in each industrial sector. It is represented in solar equivalent joules (sej) following the approach of emergy analysis [11].

The appropriate level of detail for decision making can be selected by the decision maker according to the type of decision-making task. For example, upper-level management may prefer using the most aggregated numbers, whereas process engineers may prefer the details provided by the bottom levels of the hierarchy. More aggregated metrics may be used for quick screening between alternatives.

4. CASE STUDY: AMMONIA PROCESS

This case study demonstrates use of the proposed hierarchical environmental sustainability metrics by application to an ammonia process. It provides the detailed procedure for the calculation of metric values for

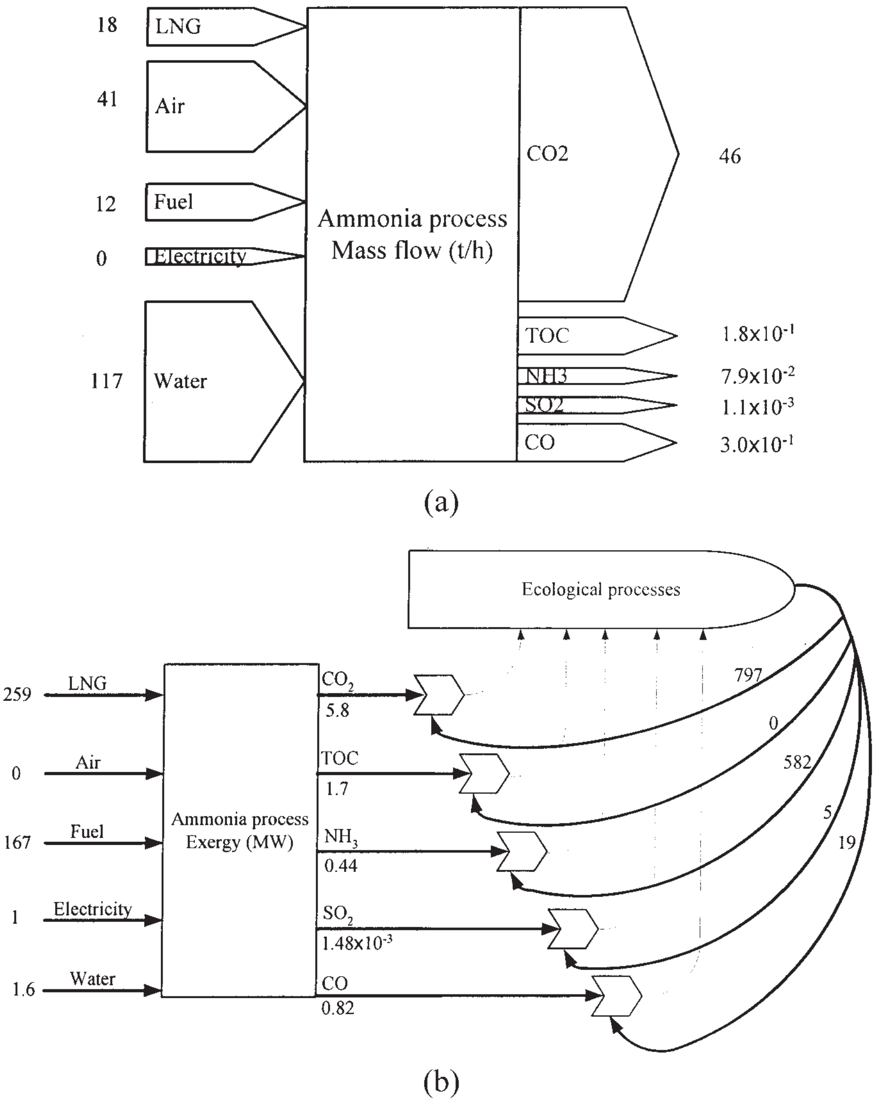

Figure 4. (a) Mass flow diagram for an ammonia process. The energy value for 12 t/h of fuel is 160 MW. (b) Exergy flow diagram for an ammonia process.

process scale, life-cycle scale, economy scale, and ecosystems scale. Detailed calculations are available in supplementary material [39].

4.1. Process Scale

Figures 4a and b show the detailed information of input and output streams for an ammonia process, based on data from Shreve and Brink [40]. From Figures 4a and b, the hierarchical metrics at the process scale are prepared very easily, as shown in Figure 5 and in Yi and Bakshi [39]. For a metric to be meaningful and permit comparison across alternatives it must be normalized by an appropriate output measure such as monetary value or exergy content. Normalized metrics may be readily obtained by dividing the numbers in Figures 4a and b by mass of ammonia (38 t/h) or its exergy (212 MW). The normalized metric value by the production rate of ammonia for material consumption at Level 1a for the ammonia process is 1.6 t/h because it includes only natural gas and air. Fuel is not included as material consumption but as an energy metric in the Level 1a. The metric value for energy consumption at Level 1a is 4.3 MW, which is the sum of net calorific

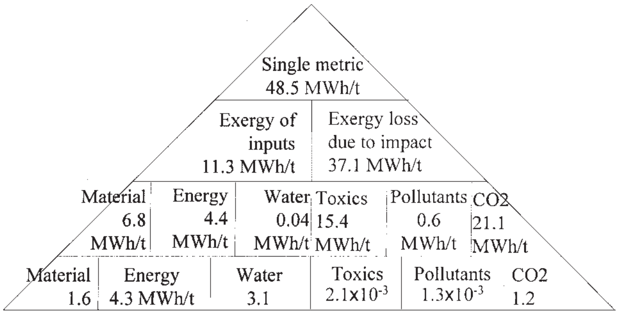

Figure 5. Hierarchy of metrics for an ammonia process. The values of metrics are normalized by the production rate of ammonia.

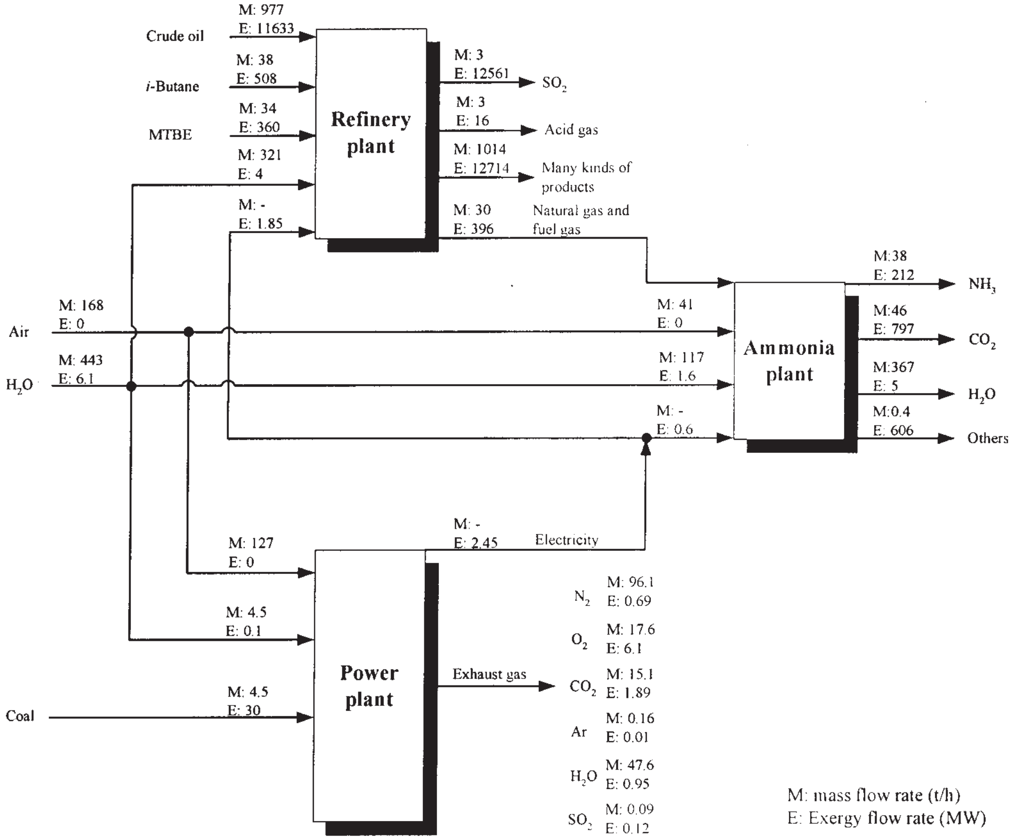

Figure 6. Mass and exergy flows for an ammonia plant and selected processes in its supply chain.

value for fuel and electric power. The value for water consumption at Level 1a is 3.1 based on assuming 10% loss of process water in a cooling tower. Exergy values for material, water, and fuel are calculated by Eq. 1, but exergy of electricity is assumed equal to its energy content. The values of emission of toxics, pollutants, and carbon dioxide are based on the work of US Department of Energy Office of Industrial Technology [41]. These emissions are converted into exergy by Eq. 3. Although the mass of emissions is much smaller than that of resource consumption, the converted exergy values of impact are three times the exergy value of input streams. The impact considers the affected systems to the end point, whereas the input exergy does not consider all the inputs to the starting point. With increasing spatial scale, this disparity decreases. The single metric in Level 3 is the sum of input exergies and exergy losses resulting from environmental impact and dissipation in Level 2.

4.2. Life-Cycle Scale

The system boundary for sustainability metrics is expanded using process-based life-cycle analysis. The expanded system includes a refinery process for the generation of natural gas from crude oil and a power plant for the generation of electric power from coal. The flow information for mass and exergy is based on data from Maple [42] and Taftan Data (www.taftan.com). Such information could also be obtained from commercial life-cycle inventory databases. Natural gas is produced in the refinery from crude oil, and is fed to the ammonia plant as raw material. Electric power for the ammonia plant is supplied from the power plant where coal is consumed to generate electricity. Figure 6 shows input and output flows of material and exergy for the process-based life-cycle scale. From Figure 6, sustainability metrics for individual processes of the power plant, refinery, and ammonia plant are shown at the process scale in Figure 7. The calculation procedures for the refinery and power plant are similar to those for the ammonia plant [39].

Figure 7 shows the normalized hierarchical metrics for life-cycle scales of an ammonia process. The hierarchical metrics of a power plant and a refinery plant at process scale are normalized by the production rate of electricity and natural gas, respectively. However, the hierarchical metrics in process-based life-cycle scale, economic scale, and ecological scale are normalized by the production rate of ammonia. Therefore, the hierarchical metrics of a power plant and a refinery plant are multiplied by production rates of electricity and natural gas to prepare the hierarchical metrics at coarser scales. The material metric value in Level 1a for the life-cycle scale is 32.2, which is calculated from the flow rates of crude oil, *i*-butane, MTBE, and air. The corresponding energy value at Level 1a for the life-cycle scale is 0.7 MWh/t, which corresponds to a net calorific value of 0.12 of coal. The water metric value at Level 1a for the life-cycle scale is about 11.7 with the 10% loss of cooling water. Emission flow rates at this scale are obtained

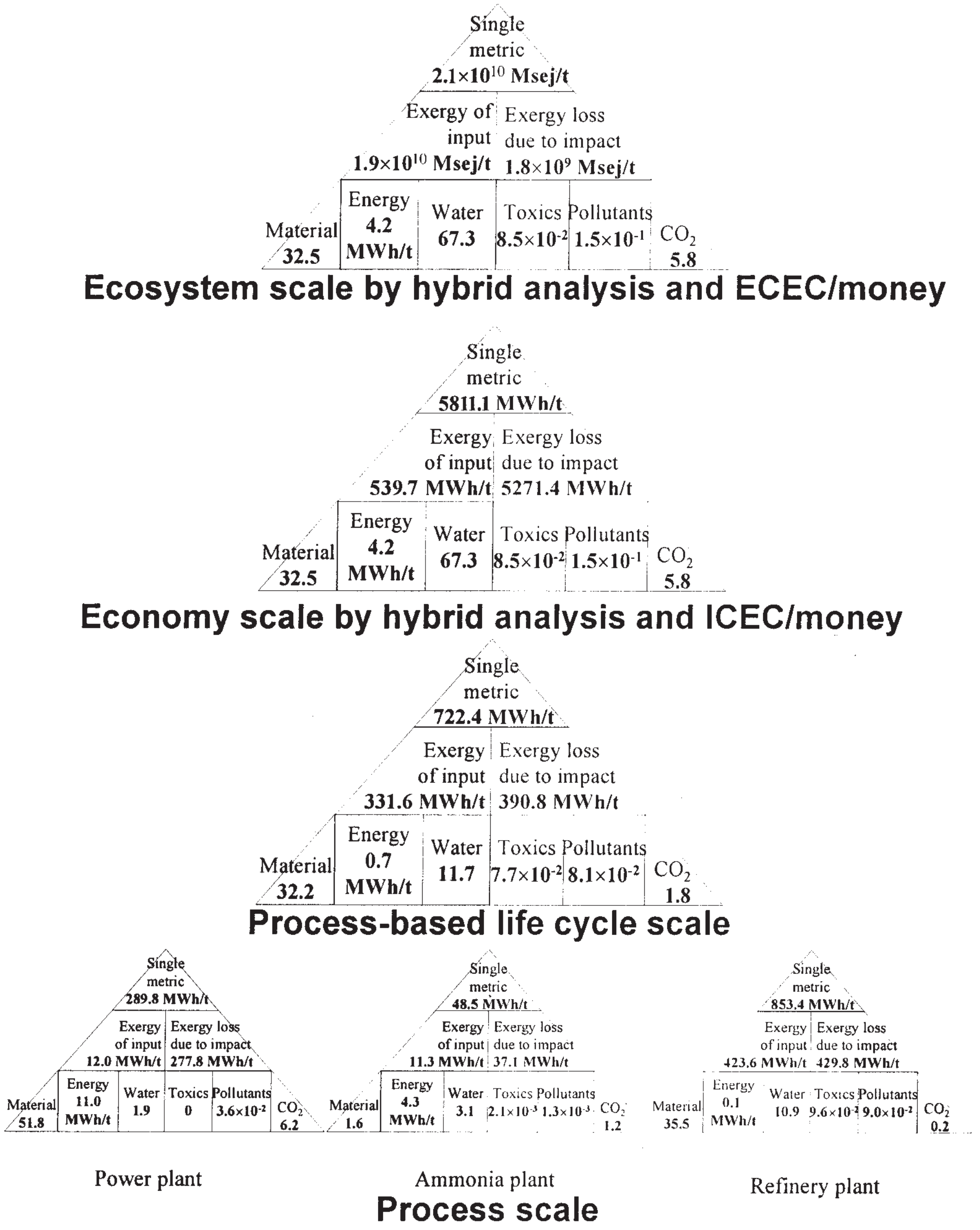

Figure 7. Multiscale hierarchy of sustainability metrics for ammonia process. The values of metrics are normalized by the production rate of ammonia.

by addition of this information at the finer scale, and exergy values of input streams and exergy loss attributed to impact are calculated as for the ammonia plant. Not surprisingly, the exergy consumption at the life-cycle scale of an ammonia process is larger than that for the single ammonia process. The input-side metric for the entire life-cycle scale of an ammonia process is about 30 times larger than that for the ammonia process alone, whereas the output-side metric of this scale is 10 times larger than that of the ammonia process only. However, the analysis is still incomplete because the contribution of the rest of the life-cycle network is ignored at the process-based life-cycle scale.

4.3. Economy Scale

The incompleteness of process-based LCA may be addressed by a thermodynamic hybrid life-cycle analysis based on the ICEC to money ratios discussed in section 3. The economy scale in Figure 7 shows the results by hybrid life-cycle analysis of an ammonia process. The metric values of Level 1a at the economy scale at Figure 7 are the sum of the process-based life-cycle analysis and of applying EIO-LCA to cutoff streams at the life-cycle scale. These include crude oil, *i*-butane, MTBE, and coal. For each cutoff stream, the corresponding economic sector is selected for applying

EIO-LCA. This approach results in information about consumption of energy, water, and ores and production of pollutants, green house gases, toxics, and so forth in the entire economy, which are added to those from process-based LCA to give metric values in Level 1a of the economy scale. Exergy at Level 2 is the sum of exergy consumption and exergy losses arising from impacts by process-based analysis and by EIO-LCA. The exergy consumption by process-based analysis is shown in Figure 7, which is calculated by Eq. 1. The exergy consumption by EIO-LCA is calculated by Eq. 4. For example, the ratio of ICEC to money for the sector of coal mining is 2.03×10^9 J/\$. This is used to estimate the total ICEC consumption in the economy ascribed to the coal consumption of 0.12 t/h at the cost of 5 \$/t. The ratios of ICEC to money are available for each US economic sector in Ukidwe and Bakshi [25]. Exergy loss attributed to impact is calculated by Eq. 3 and DALY values of emission materials. For example, the emission of carbon dioxide is 5.8 t/h and its DALY value is 2.1×10^{-7} DALY/kg. The converting coefficient ξ of carbon dioxide is 3.1×10^{14} J/DALY, which is available from Ukidwe and Bakshi [25]. Therefore, exergy loss due to emission of carbon dioxide is about 104.9 MW. The exergy losses for other streams can be calculated in the same way.

The exergy of input streams at the economy scale is smaller than exergy loss resulting from impact, which means that cumulative exergy consumption by all processes to make ammonia is smaller than the potential exergy changes in the environment by waste emission. In addition, energy consumption, water consumption, and carbon dioxide emission are substantially increased compared with the metric values of process life-cycle scale. Including the entire economy for life-cycle analysis is not complete because ecological products and services are indispensable for industrial and economic activities and need to be included in the analysis.

4.4. Ecosystem Scale

ECEC analysis expands the system boundary of ICEC to include all ecological processes required to make natural resources available to industries [27]. The ECEC values for inputs and impact of emissions may be readily obtained by an approach similar to that used for the economy scale in section 4.3. The ECEC to money ratio for sectors of the U.S. economy [25] are used instead of the ICEC to money ratios. ECEC is represented by a consistent thermodynamic unit of solar equivalent joule (sej) and is calculated for the streams in Level 2 of the ecosystem scale by the ratio of ECEC to money for each economic sector by Eq. 5. Alternatively, the ECEC to ICEC ratio of each sector may be used. For example, ICEC consumption of 0.12 t/h of coal is 0.18 MW, and is converted to ECEC by multiplication with the ECEC/ICEC ratio of 19,001 sej/J, resulting in the ECEC of about 3420 Msej/s. The exergy loss resulting from impact by emissions in Level 2 for the ecosystem scale is calculated by multiplying the output-side metrics of Level 2 in the economy scale by the ratio of ECEC/ICEC for U.S. economic sectors, which is also available in Ukidwe and Bakshi [25]. The cumulative exergy values at the ecosystem scale are much larger compared with those of the economy scale because energy is required to make natural product and/or services by ecological processes. When raw materials are made from ecological processes, exergy is consumed or lost. Therefore, the exergy consumption during ecological processes is not negligible when sustainability of industrial processes is evaluated. The ratio of ECEC to money is based on the consumption of the ecological exergy when the environmental sustainability of a process is evaluated.

5. DISCUSSION AND CONCLUSIONS

Quantification of environmental sustainability is important for sound engineering and strategic decision making. A variety of sustainability metrics developed by various academic and industrial groups rely on quantifying the material and energy flow and impact of emissions. Such metrics suffer from the curse of dimensionality, may lack adequate scientific rigor because of ignorance of the second law, and often fail to address the multiscale nature of environmental challenges. This paper proposes the use of thermodynamic methods combined with input–output and hybrid life-cycle assessment to overcome these shortcomings. Exergy analysis is used for scientifically rigorous combination of material and energy streams, and the quantification of emission impacts. These results are represented by an aggregation hierarchy for the selected system. Evaluation of sustainability requires such aggregation hierarchies at multiple spatial scales including, process, life cycle, economy, and ecosystem, resulting in a doubly nested tree of metrics. Expansion to coarser spatial scales is achieved by the thermodynamic input–output analysis approach of Ukidwe and Bakshi [25]. The appropriate level of analysis may be selected depending on user preference and the type of analysis.

The focus of this paper is on the use of thermodynamic and multiscale methods for improving existing practical metrics such as those developed by AIChE–CWRT [7]. The goal of any metric is to compare alternatives and guide decision making. Detailed empirical study is essential for evaluating various kinds of thermodynamic metrics, and is the subject of on-going work. The suitability of normalization by the monetary, exergetic, or some other value of the outputs also requires more study. The proposed thermodynamic methods may also be improved, particularly for evaluating the impact of emissions. This work relies on Eco-indicator 99 and considers only the human impact of emissions. Similar methods are needed for evaluating the impact on ecosystems more completely.

The focus of this paper has been mainly on metrics for environmental sustainability. However, sustainability requires consideration of ecological, economic, and social aspects. The proposed metrics based on exergy seem to be capable of considering all the three dimensions, given that exergy is the ultimate limiting resource for all economic and ecological activities. Such metrics are also referred to as 3-D metrics [5]. The aggregated exergy-based metrics at Level 3 may be useful as 3-D metrics, whereas metrics at lower levels could be 2-D and 1-D metrics. For example, exergy consumption by inputs is an effective 2-D indicator of economic and ecological efficiency. Thus, the proposed framework may permit decision making over a hierarchy that considers 3-D metrics for quick screening followed by smaller-dimension metrics. Techniques for multiobjective decision making and handling uncertainty will also need to play an essential role in the practical use of the proposed metrics.

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