# Assessment of Sustainability-Potential: Hierarchical Approach

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Our capability to conceive or identify alternative synthetic routes, i.e., reaction paths, to manufacture a single or set of chemical compounds from various precursors is being enhanced acceleratedly. This has been brought about by the availability of ever expanding chemical databases and the advent of efficient modern experimental techniques and computational methods. In the current intensely competitive economic environment, we need to avail ourselves of the mechanisms or tools to speedily weed out those alternative synthetic routes that might generate unequivocally unprofitable processes prior to initiating costly developmental efforts. The gross-profit or profit-potential estimation is one of such tools; it evaluates the potential profit from each synthetic route as the difference between the prices of the final reaction products and starting reactants for manufacturing a unit quantity of the desired product (Rudd et al., 1973; Meyers and Seider, 1975; Biegler et al., 1997; Seider et al., 2004). Nevertheless, it is totally untenable to scale–up a process even if the profit-potential is estimated to be exceedingly large when its operation is unsustainable.

The sustainability of a chemical process has been variously defined. In general, however, its assessment entails the consideration of such factors as energy and material requirements; safety and health effects; ecological and environmental impacts; and societal and regulatory constraints (Anastas et al., 1998; Sikdar and Howell, 1998; Allen and Shonnard, 2001; Hertwig et al., 2002). The thermodynamic performance of and the profit from the process of concern are largely dependent on its energy and material requirements; moreover, both of them are quantifiable. The thermodynamic performance can be evaluated through the energy and available energy balances around the process, in general, and through the latter, in particular. The available energy balance results from the combination of the first and second laws of thermodynamics (Keenan, 1951; Hatsopoulos and Keenan, 1965; Denbigh, 1966; Szargut and Petela, 1965; Szargut et al.,1988; Fan and Shieh; 1980; Petit and Gaggioli,1980; Sussman, 1980; Fan et al.,1983; Kenney, 1984). In reality, however, it also implicitly embodies the mass conservation law: The available energy balance entails the detailed accounting of every material species involved in the process. This renders it possible to determine the transformation of its inherent available energy pertinent to its chemical changes, which is termed chemical exergy.

Exergy, comprising physical, thermal, and chemical exergy, is measured relative to the dead state or extended standard state defined by the environmental temperature, the environmental pressure, and the datum level substances. Any element is part of the corresponding datum level substance, which is thermodynamically stable, exists in abundance, and contains no available energy (Denbigh, 1966; Fan and Shieh; 1980; Keenan, 1941; Gaggioli, 1961; Reistad, 1970; Debenedetti, 1984). The environmental temperature and pressure, which vary according to time and place, are usually adopted as the datum level temperature and pressure; nevertheless, they are often specified as 298 K and 1 atm, respectively, for convenience and also to be consistent with the conventionally-defined standard state. Note that the system's available energy, or exergy, depends on the extent of its deviation from the dead state, i.e., the extended standard state. In other words, any deviation (the physical, thermal and/or chemical deviations) of the state of the system from the dead state, induced by physical, thermal and/or chemical processes, gives rise to the system's available energy.

Substantial progress has been made to quantify the safety and health effects in terms of the toxicity indices of the materials to be involved in the process, even though the values of these indices are more nebulous than those of exergies and costs. This is also the case for the ecological and environmental impacts; fortunately, the process' thermodynamic performance in terms of the exergy dissipation due to the reaction is one of the effective indicators of the thermal and material dissipations due to the reaction involved. The societal and regulatory constraints are least amenable to quantification; nevertheless, much effort is being spent to quantify them by social and political scientists and economists.

A hierarchical approach is proposed here to assess the sustainability of a chemical process based on any of the alternative synthetic routes. This novel notion of sustainability-potential is a generalization of the notion of profit-potential (Fan et al., 2002). Analogous to the profit-potential, the sustainability-potential is estimated from the reaction products and starting reactants of the synthetic route. Alternative synthetic routes yielding a reaction product or a set of reaction products, however, tend to form a complex reaction network: These synthetic routes often share some common starting reactants and intermediates. It is indeed daunting to completely recover all the individual feasible synthetic routes from the network. This difficulty can be overcome by identifying them by resorting to a highly efficient algorithmic method for network synthesis based on process graphs (P-graphs) at the outset of assessment (Friedler et al., 1992a, 1992b, 1993, 1996 and 1998; Imreh et al., 1997). The two fundamental algorithms of this P-graph-based approach, i.e., algorithms MSG for the maximal structure generation and algorithm SSG for the solution structure generation, collectively yield combinatorially feasible synthetic routes. These synthetic routes are further screened to identify feasible synthetic routes, generally in the form of reaction networks, in the light of the molar-balance constraints via linear programming by minimizing the linear sum of integer multipliers for the stoichiometric expressions of individual reactions in each combinatorially feasible synthetic route (reaction network). Furthermore, any of the feasible synthetic routes generated is assessed through the sustainability-potential, which is outlined in what follows.

The individual feasible synthetic routes yielding the desired product are hierarchically or sequentially assessed in descending order of quantifiability. In the first step, the synthetic routes are assessed in terms of the exergy dissipation, subject to a criterion specified on the

basis of the extent of dissipation. In the second step, those synthetic routes surviving the scrutiny of the first step are assessed in terms of the profit-potential, subject to a criterion specified on the basis of the size of profit. In the third step, those synthetic routes surviving the scrutiny of the first two steps are assessed in terms of the toxicity indices, subject to a criterion specified on the basis of the magnitude of toxicity indices. Naturally, the assessment can proceed further as the ecological and environmental impacts and/or the societal and regulatory constraints become sufficiently quantifiable. It is worth noting that the first step of assessment in light of exergy dissipation should be of the most fundamental and practical significance; the second step, the next most; and so on. The efficacy of the proposed hierarchical approach is illustrated with an example. An effort is being made to render it possible to execute hierarchical assessment of sustainability-potential online.

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