

Assessment of Sustainability-Potential: Hierarchical Approach

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A hierarchical approach is proposed to estimate the sustainability-potential 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, the estimation of which renders it possible to screen out economically nonviable processes derived from the alternative synthetic routes at the earliest stage. At the outset of assessment, all the individual alternative synthetic routes are identified by the graph-theoretic method based on process graphs (P-graphs). Subsequently, the individual alternative synthetic routes are sequentially assessed in descending order of quantifiability, in terms of available energy (or exergy), dissipation, the possible profit, and the toxicity index, respectively. The efficacy of the approach is demonstrated for the manufacture of C_2H_3Cl . The approach can possibly be adapted for estimating the sustainability-potential to assess the alternative production routes as represented by alternative flowsheets for manufacturing specific products.

1. Introduction

Our capability is being acceleratedly enhanced to conceive or identify alternative synthetic routes, i.e., reaction paths, to manufacture a single or set of chemical compounds from various precursors (starting reactants). This has been rendered possible by the availability of ever-expanding chemical databases, and the advent of efficient modern experimental techniques and computational methods.^{1–5} In the current intensely competitive economic environment, we need to avail ourselves of the means to speedily weed out those alternative synthetic routes that might generate unequivocally unprofitable processes prior to initiating costly developmental or design efforts. The gross-profit or profit-potential estimation is one such means, which was conceived originally by Rudd and his colleagues.⁶ The profit-potential is estimated under the most ideal conditions, where the reactants are totally converted into the reaction products. It evaluates the potential profit from each alternative synthetic route as the difference between the prices of the final reaction products and those of starting reactants for manufacturing a unit quantity of the desired product.^{6–9} The estimation of profit–potential renders it possible to screen out nonviable processes derived from the alternative synthetic routes at the earliest possible stage, i.e., the conceptualization or laboratory-experimentation stage, prior to proceeding to the pilot-scale development and/or preliminary design, thereby preventing the enormous expenditure that might be incurred for such effort. It is worth noting that the possibility or probability of any of the reaction paths (synthetic routes) rejected under the most ideal conditions to surface as viable ones in the detailed design stage would, indeed, be nil. Nevertheless, even if the profit-potential is estimated to be exceedingly large, it is totally untenable to scale up a process when its operation is unsustainable.

The sustainability of a chemical process has been variously defined. Generally, its assessment entails the consideration of

many factors: energy and material requirements; costs and profits; safety and health effects; ecological and environmental impacts; and societal concerns and regulatory constraints,^{10–14} all of which are essentially the focuses of the emerging field of industrial ecology.^{15,16} The thermodynamic performance of (and profit from) the process of interest are largely dependent on its energy and material requirements; moreover, both of them are quantifiable.

The thermodynamic performance generally can be evaluated through the energy and available energy balances around the process, and through the latter, in particular. The available energy balance results from the combination of the first and second laws of thermodynamics.^{17–25} 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 requirement renders it possible to determine the transformation of its inherent available energy pertinent to its chemical changes, which is termed chemical exergy. Exergy, which is composed of physical, thermal, and chemical exergy, is measured relative to the dead state or extended standard state (see Appendix A in the Supporting Information).^{20,21,26–29} Note that the system's available energy, or exergy, is dependent on the extent of its deviation from the dead state, i.e., the extended standard state. In other words, any deviation is measured of the system's physical, thermal, and/or chemical state from the dead state.

Substantial progress has been made to quantify the safety and health effects, in terms of the toxicity indices of the materials involved in the process, even though the values of these indices are more nebulous than those of exergy and cost. The least amenable to quantification are the ecological and environmental impacts or the societal and regulatory constraints; nevertheless, much effort is being spent to quantify them.^{14,30,31} Fortunately, the thermodynamic performance of the process, in terms of the exergy dissipation due to the reaction, is one of the effective

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Table 1. Chemical Exergies, Unit Prices, and Toxicity Indexes of the Reacting Species in the Overall Reactions of All Alternative Synthetic Routes for the Manufacture of Vinyl Chloride (C₂H₃Cl)

reacting species and its phase at the standard state	boiling point (°C)	chemical exergy, ε ⁰ (kcal/g-mol)	unit price, ^a ζ (¢/lb)	toxicity index, tid
Starting Reactants				
C ₂ H ₄ (gas)	-103.7	324.00	36	4
C ₂ H ₂ (gas)	-80.8	301.24	64	
Cl ₂ (gas)	-34.04	123.8	17	4
O ₂ (gas)	-182.95	0.9263	0	5
HCl (gas)	85.1	1980.79	4	4
Target Reaction Product				
C ₂ H ₃ Cl (gas)	-13	353.12	36	1
Reaction Byproduct				
H ₂ O (liquid)	100	0	0	5

^aThe prices are averaged values obtained from *Chemical Market Reporter*, January 3, 2005, Vol. 267, No. 1, pp 20–22, except for acetylene's price, which is from a different issue (i.e., *Chemical Market Reporter*, January 17, 2005, Vol. 267, No. 3, p 31).

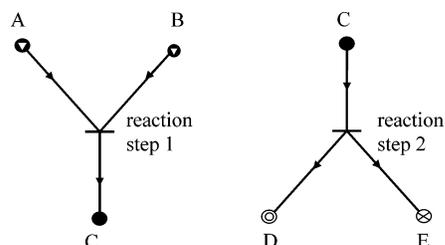


Figure 1. Process graph (P-graph) representations of reaction step 1 (A + B → C) and reaction step 2 (C → D + E), and participating reacting species (A, starting reactant; B, starting reactant; C, intermediate; D, target reaction product; and E, reaction byproduct).

indicators of the extent of thermal and material losses. Specifically, exergy dissipation leads to available energy loss in the form of heat as well as to reacting-species loss in the form of pollutants to the surrounding environment; the former gives rise to thermal pollution, and the latter, to material pollution. Obviously, these losses invariably increase the cost of the process, thereby reducing the profit-potential; however, the reverse is not true. The profit-potential is also influenced by the artificial manipulation of the market. Moreover, the loss of material species to the surrounding environment as pollutants inevitably magnifies the risk and reduces the safety of operating the process.

A hierarchical approach is proposed herein to assess the sustainability-potential of a chemical process crafted from any of the alternative synthetic routes. This novel notion of sustainability-potential is a generalization of the notion of profit-potential.^{6–9} Analogous to the profit-potential, the sustainability-potential is estimated from the reaction products and starting reactants (precursors) of each of the alternative synthetic routes.

Alternative synthetic routes that yield a reaction product or a set of reaction products, however, have a tendency to form a complex reaction network: Such alternative synthetic routes often share some common starting reactants and intermediates. It can be a daunting task to recover completely all the alternative synthetic routes from the network. This difficulty can be overcome by identifying them at the outset of assessment by resorting to a highly efficient graph-theoretic, algorithmic method for network synthesis based on process graphs (P-graphs).^{32–37} Subsequently, each of the alternative synthetic routes generated is assessed by estimating its sustainability-potential, which is outlined in the following discussion.

The individual alternative synthetic routes that yield the desired product or products are hierarchically or sequentially

assessed in descending order of quantifiability. In the first step, all the synthetic routes are assessed in terms of the exergy dissipations, 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 expected 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 the toxicity indices. Naturally, the assessment can proceed further as the ecological and environmental impacts and/or the societal concerns and regulatory constraints become sufficiently quantifiable, which is beyond the scope of the current work. It is worth noting that the first step of assessment in light of exergy dissipation should be of the most fundamental and practical significance, because of its firm theoretical foundation; the second step, the next most; the third step, the third most; and so on. The efficacy of the proposed hierarchical approach is demonstrated with a well-known example of manufacturing vinyl chloride (C₂H₃Cl).^{9,38–42}

2. Methodology

The methodology comprises two parts. One involves the exhaustive identification of alternative synthetic routes. The other estimates hierarchically the sustainability-potential of each of the resultant individual alternative synthetic routes, in light of the criteria including the extent of available energy or exergy dissipation, potential profit, and toxicity index.

An individual alternative synthetic route yielding the desired product or products involves one or more distinct reaction steps, each requiring its own separate reaction space, or reactor. The reaction products from any reaction steps, which serve as the reactants of the succeeding reaction step, are intermediates. Obviously, only the starting reactants (precursors) are fed into any of the reaction steps from the external environment and the final reaction products are discharged to the external environment; thus, their quantities must be taken into account in assessment.

It is worth noting that adjusting each reaction step to eliminate intermediates and algebraically summing the production and consumption of each reacting species yield the net stoichiometry of the synthetic route. This net stoichiometry can be regarded as the stoichiometry of the composite overall reaction embodying all the reaction steps, or simply the overall reaction, involving only the starting reactants (precursors) entering into the synthetic route at any reaction step and the final reaction products emerging from the synthetic route at any reaction step. Generally, these final reaction products comprise one or more of the target products and byproducts.

2.1. Determination of Alternative Synthetic Routes. All the individual alternative synthetic routes that yield the specific desired product, which form a complex reaction network, are identified by resorting to a highly efficient algorithmic method for network synthesis, based on process graphs (P-graphs).^{32,34,36,37,42} The foundation of this algorithmic method, which is combinatorial or graph-theoretic in nature, is comprised of three cornerstones: a novel graph representation, in terms of P-graphs; a set of rigorous axioms, portraying the unique structural features of process networks (reaction networks); and a set of exact algorithms.^{32–36,43} A compact and exact presentation of all alternative synthetic routes, each comprising a reaction network, can be accomplished effectively by constructing the complete network of reaction steps possibly contained in such alternative synthetic routes; i.e., all the combinatorially feasible

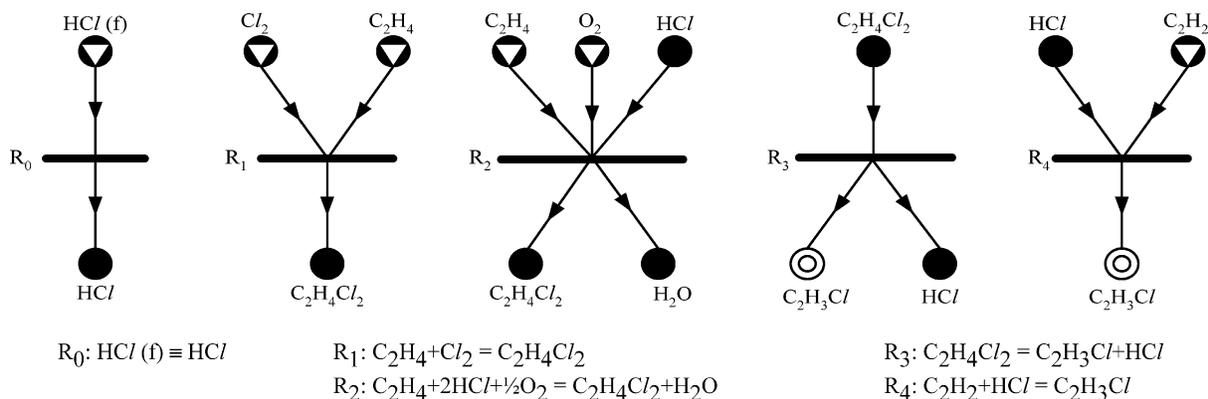


Figure 2. P-graph representations of reaction steps R_0 – R_4 .

reaction network can be extracted from the maximal structure of reaction network. Finally, the alternative synthetic routes are identified from these combinatorially feasible reaction networks as the feasible reaction networks, which can range from simple sequences of reaction steps to complex sequences of reaction steps that contain one or more loops and/or branches.

Every reaction step is a functional unit for material transformation, and thus it is an operating unit; naturally, starting reactants, intermediates and final reaction products are materials in the phraseology of P-graphs. Note that, after one or more of the final reaction products are specified as the target reaction products, those that remain are regarded as the reaction byproducts.

2.1.1. P-Graph Representation. A P-graph is a directed bipartite graph (i.e., digraph); it is comprised of two types of vertices or nodes.^{32–33} Figure 1 illustrates the components of a P-graph; one type, which has circles as their symbols, is of the M-type, representing materials, which are reacting species in the context of reaction-network synthesis, and form set m , and the other, with horizontal bars as their symbols, is of the O-type, representing operating units, which are reaction steps in the context of reaction-network synthesis, and form set o . For convenience, the four classes of circles are defined as the symbols for the vertices representing reacting species. They include starting reactants, intermediates, byproducts, and target products, even though the last two are both final reaction products. An arc, with an arrow indicating the direction of any reaction step, is either from a vertex signifying a reacting species to that signifying a reaction step or vice versa. Thus, a P-graph can be defined as a pair (m, o) whose vertices are the elements of the union, i.e., combination, of set m of reacting species and set o of reaction steps.

2.1.2. Axioms. P-graph (m, o) represents a combinatorially feasible reaction network, leading from the starting reactants to the final reaction products, if it satisfies axioms S1–S5, which are stated in parlance of reaction-network synthesis or discovery of alternative-synthetic-routes as given below.^{32–36}

(S1) Every final reaction product is represented in the graph.

(S2) A vertex of the M-type has no input if and only if it represents a starting reactant.

(S3) Every vertex of the O-type represents a reaction step defined in the reaction-network synthesis problem.

(S4) Every vertex of the O-type has at least one path leading to a vertex of the M-type representing a target product.

(S5) If a vertex of the M-type belongs to the graph, it must be an input to or output from at least one vertex of the O-type in the graph.

Axiom S1 implies that each product is produced by at least one of the reaction steps in the system; axiom S2 indicates that

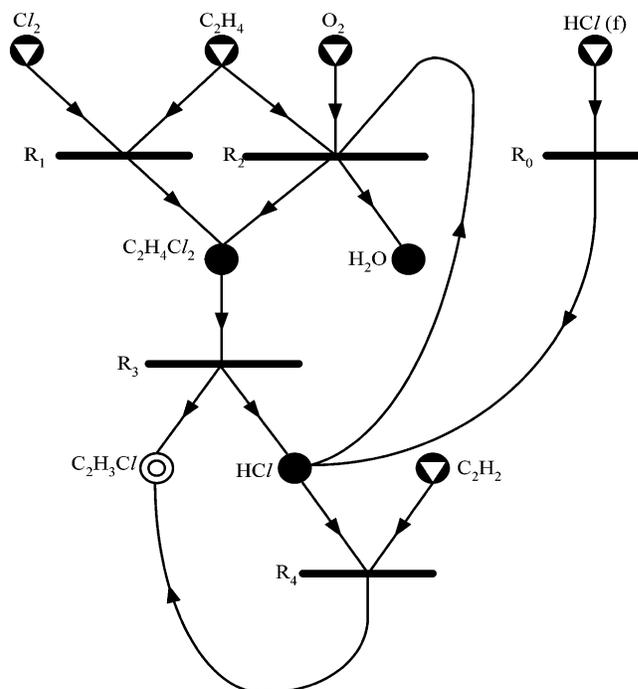


Figure 3. Maximal reaction network.

a reacting species is not produced by any reaction step of the system if and only if it is a starting reactant; axiom S3 shows that only the plausible reaction steps of the problem are taken into account in the synthesis; in axiom S4, any reaction step of the system has a series of connections, eventually leading to the reaction step that generates at least one of the final reaction products; and axiom S5 shows that each reacting species appearing in the system is an input to or an output from at least one reaction step of the system.

Note that each of the axioms evidently satisfies the dictionary definition of axiom, because it is simply the restatement of the definition of a terminology, e.g., starting reactant or final reaction product; the statement of a totally logical relationship; and/or a consequence of the law of conservation of mass. Each axiom by itself may sound innocent and useless in practice. Nonetheless, the five axioms collectively act as a filter to eliminate all combinatorially infeasible or invalid reaction networks that are invariably included in the superstructure.

2.1.3. Algorithms. The aforementioned P-graph representation and axioms create two inordinately efficient algorithms that are necessary to perform the synthesis of feasible reaction networks corresponding to the alternative synthetic routes. These algorithms are outlined in the following subsections.

2.1.3.1. Algorithm MSG, for Generating the Maximal Structure of Reaction Networks. To minimize the computational difficulty encountered in synthesizing reaction networks, their mathematical formulations should be of minimum complexity. In the framework of our approach, this is accomplished by generating the maximal structure of reaction networks, which contains exclusively all combinatorially feasible reaction networks, each leading from the starting reactants to the final reaction products, without violating the aforementioned axioms (S1–S5). Thus, the maximal structure of reaction networks, i.e., maximal reaction network, is the superstructure of reaction networks with minimum complexity.^{32–34}

A mathematically rigorous algorithm for generating the maximal reaction network, algorithm MSG, systematically places all the candidate reaction steps and examines their combinatorial feasibility in light of axioms S1–S5. The computational steps required by this algorithm do not exceed $[n_m(n_m + 1)n_0]$, where n_m and n_0 are the numbers of reacting species and reaction steps involved, respectively; thus, algorithm MSG is polynomial in nature.^{32–34}

The implementation of algorithm MSG involves two major phases; for convenience, the initial reaction-network structure is constructed at the outset by linking all common nodes representing the reacting species in the form of solid circles in P-graphs of plausible or candidate reaction networks. In the first phase, the reacting species and reaction steps that must not belong to the maximal reaction network are eliminated, stepwisely and layer by layer. The procedure is initiated at the deepest layer, i.e., starting-reactant end, of the input structure by assessing alternatively the nodes (vertices) in a reacting-species layer with those in the succeeding reaction step layer to ascertain that none of the nodes violates one or more of the five axioms. In the second phase, the nodes (vertices) are linked, again stepwise and layer by layer, starting from the shallowest end (i.e., the final reaction-product end) of the remaining input structure by assessing if any of the linked nodes violates one or more of the five axioms.

2.1.3.2. Algorithm SSG, for Generating Solution Structures Corresponding to Combinatorially Feasible Reaction Networks. The maximal reaction network generated by algorithm MSG, which itself is combinatorially feasible, contains exclusively all the solution structures corresponding to combinatorially feasible reaction networks that are capable of yielding the desired final reaction products from the given starting reactants. The algorithm for solution-structure generation (algorithm SSG) recovers all such combinatorially feasible reaction networks from the maximal reaction network.^{32–34} As mentioned previously, this algorithm is also established on the basis of the aforementioned five axioms; its details are available elsewhere (see Appendix C in the Supporting Information).^{32,33,42}

Note that, in implementing algorithms MSG and SSG, only the starting reactants and target reaction products must be explicitly specified. Naturally, the remainders are intermediates, which may create reaction byproducts when not consumed in any of the reaction steps in the network.

2.1.3.3. Linear-Programming Algorithm for Determining Stoichiometrically Feasible Reaction Networks (Synthetic Routes). Any combinatorially feasible reaction network is infeasible if the stoichiometry of the resultant overall reaction is violated. The molar balances of the overall reaction to be satisfied collectively by all the reaction steps can be ascertained through linear programming (LP) (more specifically, integer linear programming (ILP)) by minimizing the linear sum of

positive integer multipliers for the valid stoichiometric expressions of individual reaction steps subject to the molar-balance constraints. A variety of effective software is available for implementing LP; many of such software include the option for ILP. For convenience, public domain software available via the Internet at www.lindo.com is adopted in the present work. The resultant feasible reaction networks naturally constitute the alternative synthetic routes. As indicated previously, feasible reaction networks are indeed alternative synthetic routes. Note that the execution of LP as outlined herein accomplishes the aforementioned elimination of intermediates, which creates the expression for the overall reaction.

2.2. Hierarchical Assessment of the Sustainability-Potential of Alternative Synthetic Routes. The sustainability-potential of every alternative synthetic route identified is hierarchically assessed subject to various criteria in descending order of perceived importance. These criteria include available energy (or exergy), dissipation, potential profit, and toxicity index; they can be quantified after a synthetic route is established.

It is supposed that the reactants (precursors) in the exact stoichiometric ratios react isothermally and are completely converted to the reaction products in an idealized reaction space, or reactor. Moreover, the individual reactants are considered to enter the reactor separately and the individual reaction products leave the reactor also separately.^{6,18}

2.2.1. Available Energy (Exergy) Dissipation. The exergy dissipation from the synthetic route i ($\Delta\epsilon_{0,i}$) is computed as the difference between the sum of chemical exergies of the final reaction products ($\sum_{\text{products}} (v\epsilon_0)_{\text{products}}$) and that of the starting reactants ($\sum_{\text{reactants}} (v\epsilon_0)_{\text{reactants}}$). Thus,

$$\Delta\epsilon_{0,i} = \sum_{\text{products}} (v\epsilon_0)_{\text{products}} - \sum_{\text{reactants}} (v\epsilon_0)_{\text{reactants}} \quad (1)$$

The mean of the $\Delta\epsilon_{0,i}$ values from all the synthetic routes is

$$\overline{\Delta\epsilon_0} = \frac{\sum_{i=1}^N \Delta\epsilon_{0,i}}{N} \quad (2)$$

where N is the number of synthetic routes; the standard deviation of the $\Delta\epsilon_{0,i}$ values from the mean is

$$\sigma_{\Delta\epsilon_0} = \sqrt{\frac{1}{N} \sum_{i=1}^N (\Delta\epsilon_{0,i} - \overline{\Delta\epsilon_0})^2} \quad (3)$$

Any physicochemical phenomenon or process, such as heat transmission into or out of the reactor to maintain isothermal conditions and mixing of the reacting species, inevitably magnifies the exergy dissipation of the isolated system where the reactor resides, according to the second law of thermodynamics, as previously mentioned. Thus, it is unlikely that any synthetic route whose $\Delta\epsilon_0$ is excessively more negative than $\overline{\Delta\epsilon_0}$ will ever be sustainable. Analogous to the statistical data analysis,^{44,45} therefore, it is deemed to be appropriate to exclude an alternative synthetic route from further consideration if the negative difference between its $\Delta\epsilon_0$ and $\overline{\Delta\epsilon_0}$ values is $(-\sigma_{\Delta\epsilon_0})$ or greater. Hence, $L_{\Delta\epsilon_0}$, which is defined as

$$L_{\Delta\epsilon_0} = \overline{\Delta\epsilon_0} - \sigma_{\Delta\epsilon_0} \quad (4)$$

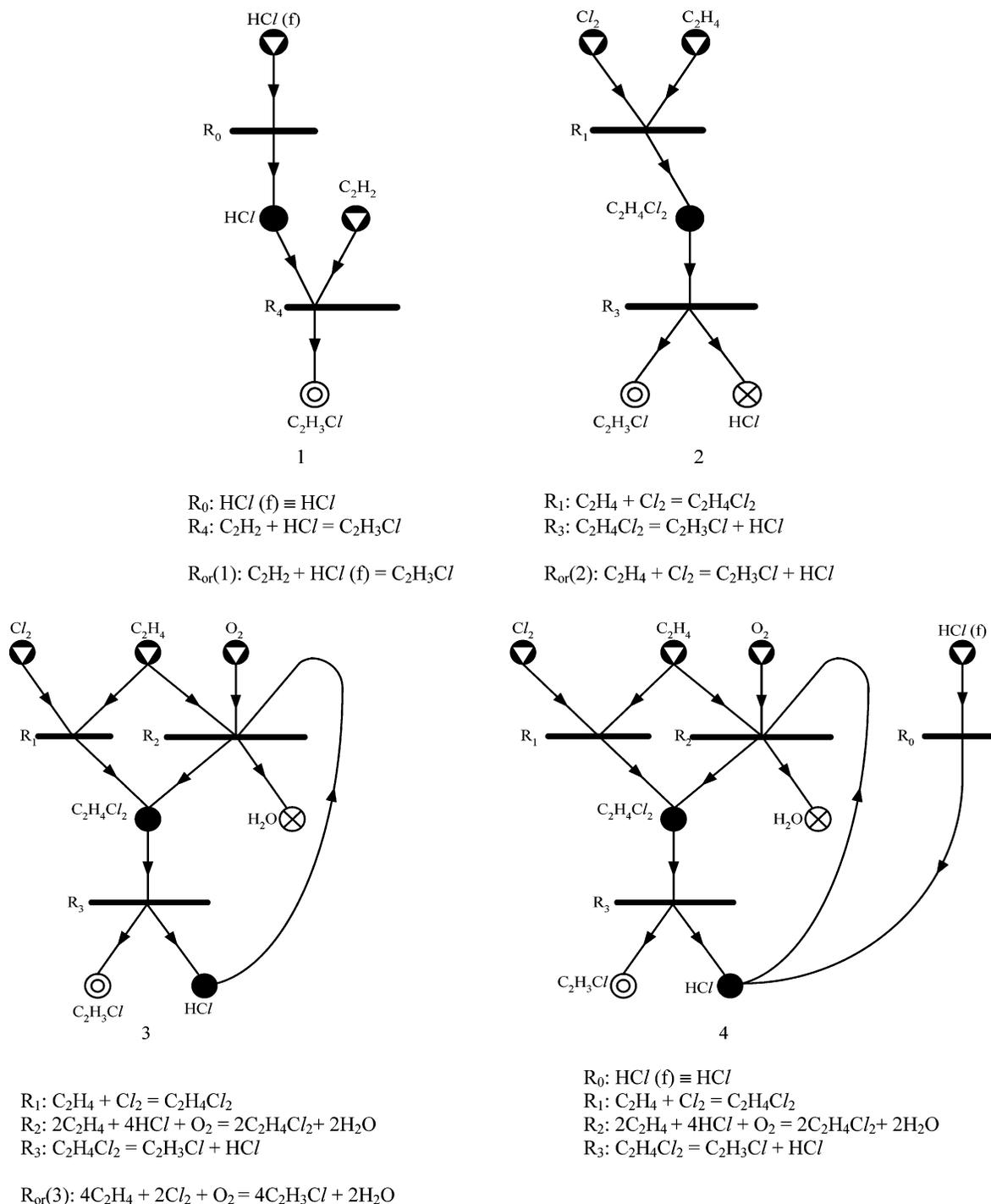


Figure 4. Combinatorially feasible reaction networks 1–4. Networks 1, 2, and 3 are also feasible; note that HCl(*f*) can be simply replaced by HCl.

could serve as the lower bound for weeding out any synthetic route on the basis of exergy dissipation.

2.2.2. Potential Profit. Each of the synthetic routes that survives the scrutiny, in light of available energy or exergy dissipation, is subsequently assessed by evaluating its potential profit (gross profit).^{6,7,9} The potential profit of any synthetic route *i* ($\Delta\zeta_i$) is computed as the revenue derived from the sales of the final reaction products, less the cost of the starting reactants, i.e., the sum of the unit prices of the pure final reaction products ($\sum_{\text{products}} (\nu\zeta)_{\text{products}}$) minus that of the pure starting reactants ($\sum_{\text{reactants}} (\nu\zeta)_{\text{reactants}}$):

$$\Delta\zeta_i = \sum_{\text{products}} (\nu\zeta)_{\text{products}} - \sum_{\text{reactants}} (\nu\zeta)_{\text{reactants}} \quad (5)$$

The prices of the pure chemicals are available in the *Chemical Marketing Reporter* (www.chemicalmarketreporter.com). A synthetic route with a positive potential profit, i.e.,

$$\Delta\zeta_i > 0 \quad (6)$$

is regarded as being sustainable and, therefore, is worthy of further assessment. Otherwise, this synthetic route is regarded unsustainable, and, hence, it is eliminated.

2.2.3. Toxicity Indices. The toxicity of every synthetic route that survives the scrutiny, in light of exergy dissipation and potential profit, can be evaluated subsequently, in terms of various toxicological properties. Such toxicological properties include carcinogenicity, irritancy, lachrymation, neurotoxicity

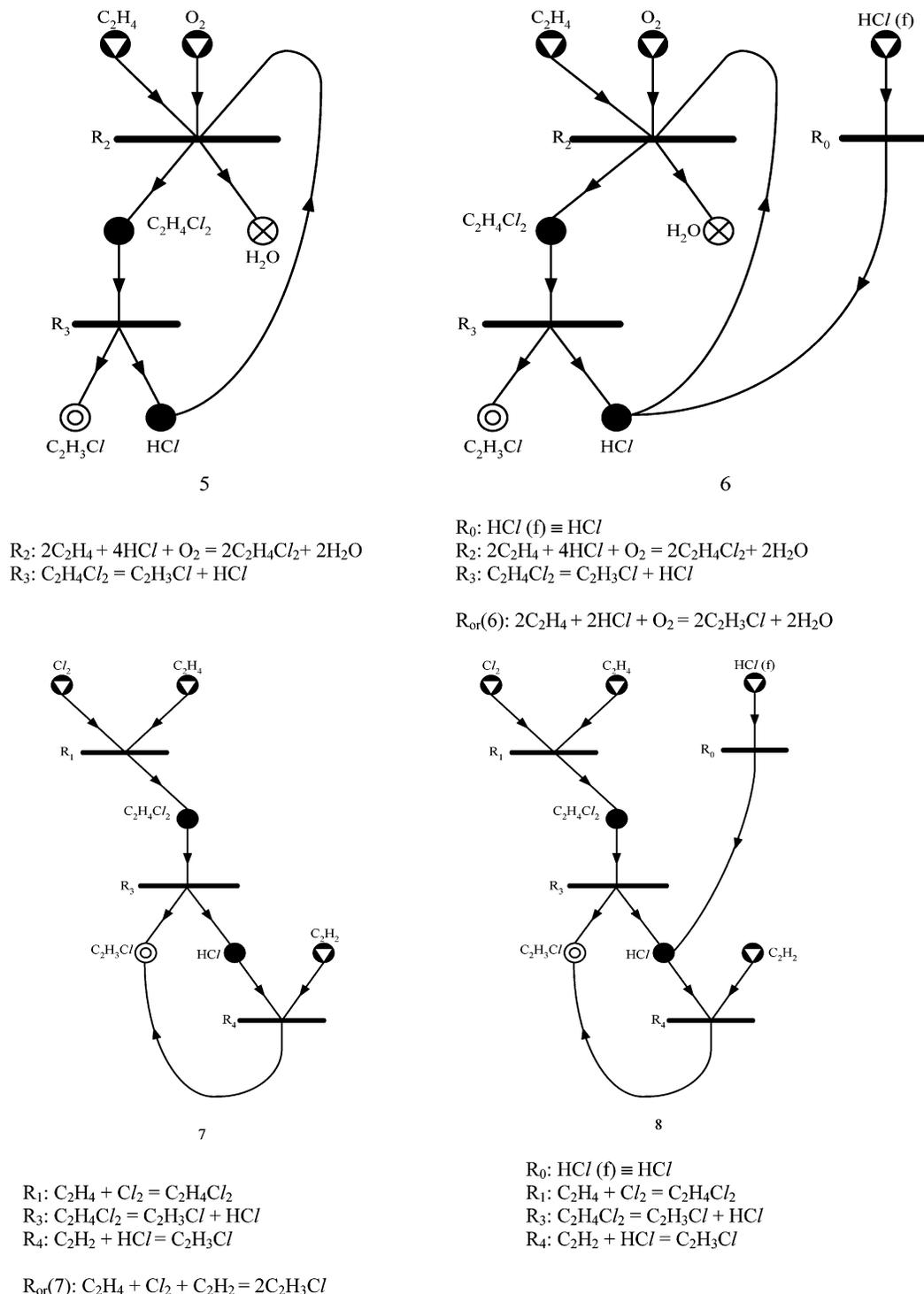


Figure 5. Combinatorially feasible reaction networks 5–8. Networks 6 and 7 are also feasible; note that HCl(f) can be simply replaced by HCl.

and thyroid toxicity, teratogenicity, respiratory and skin sensitization, and mutagenicity.^{46–49}

Numerous databases are available; among them, the National Fire Protection Association (NFPA) Hazard Rating System currently seems to be most comprehensive. Nevertheless, it is not a public domain database. For simplicity and illustration, the present work adopts a quantitative carcinogenicity database available in the public domain (<http://monographs.iarc.fr/ENG/Classification/index.php>). In this database, five groups of chemicals or reagents are assigned five indices, according to the levels of their toxicity to humans: an agent in group 1 is carcinogenic to humans; group 2A represents compounds that

are probably carcinogenic to humans; group 2B represents compounds that are also possibly carcinogenic to humans; group 3 represents compounds that are not classifiable in regard to their carcinogenicity to humans; and group 4 represents compounds that are probably not carcinogenic to humans.⁴⁹ The interface to the database, implemented for continual updating, is configured so that any existing or novel quantitative toxicity database can be incorporated into it, whenever it is deemed desirable. Naturally, the reacting species in any alternative synthetic route are reagents in the context of the current work.

For the quantitative evaluation, the toxicity index of each reacting species is 1 if it belongs to group 1, 2 if it belongs to

group 2A, 3 if it belongs to group 2B, 4 if it belongs to group 3, or 5 if it belongs to group 4. The toxicity index of a reacting species not listed in the database will be estimated from those of similar chemicals already in the database. The overall toxicity index of a synthetic route i , noted by the term TID_i , is computed as the sum of the toxicity indexes of all reacting species (tid_j) involved in its overall reaction; thus,

$$TID_i = \sum_{j=1}^{N_i} (v \cdot tid)_j \quad (7)$$

where N_i is the number of reacting species in the overall reaction of synthetic route i . The mean of the TID_i values from all the synthetic routes is

$$\overline{TID} = \frac{\sum_{i=1}^N TID_i}{N'} \quad (8)$$

where N' is the number of these synthetic routes. The standard deviation of the TID_i values from the mean is

$$\sigma_{TID} = \sqrt{\frac{1}{N'} \sum_{i=1}^N (TID_i - \overline{TID})^2} \quad (9)$$

According to the assignment of the toxicity index, the higher the toxicity index, the lower the toxicity. As a result, the greater the value of TID_i , the greater the sustainability of synthetic route i . Therefore, synthetic route i should be eliminated from further consideration if the negative difference between its TID_i and \overline{TID} values is σ_{TID} or greater.^{43–45} Hence, L_{TID} , which is defined as

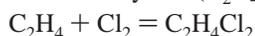
$$L_{TID} = \overline{TID} - \sigma_{TID} \quad (10)$$

could serve as the lower bound for weeding out any synthetic route on the basis of toxicity index.

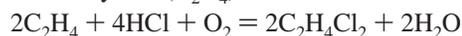
3. Example

The proposed approach is illustrated with the manufacture of vinyl chloride (C_2H_3Cl).^{9,38–42,46} C_2H_3Cl can be produced from ethylene (C_2H_4), acetylene (C_2H_2), chlorine (Cl_2), oxygen (O_2), and hydrogen chloride (HCl) through four reactions. These reactions and their stoichiometric expressions are listed below.^{9,40–42}

R_1 , direct chlorination of ethylene (C_2H_4):



R_2 , oxychlorination of ethylene (C_2H_4):



R_3 , pyrolysis of ethylene dichloride ($C_2H_4Cl_2$):



R_4 , hydrochlorination of acetylene (C_2H_2):



Note that, in constituting the network of reaction paths, or alternative synthetic routes, from these reaction steps, HCl in reactions R_2 , R_3 , and R_4 can be a starting reactant and/or an intermediate, which may create a reaction byproduct. For

differentiation, HCl that serves as the starting reactant is denoted as $HCl(f)$. For clarification, a gate reaction R_0 , which signifies the external supply of HCl , is expressed as



The reaction steps, R_0 through R_4 , will yield a variety of alternative synthetic routes for C_2H_3Cl .

3.1. Determination of Alternative Synthetic Routes. The reaction steps, R_0 – R_4 , include five starting reactants (C_2H_4 , C_2H_2 , Cl_2 , O_2 , $HCl(f)$), two intermediates ($C_2H_4Cl_2$, HCl), and two final reaction products (C_2H_3Cl and H_2O , where the former (C_2H_3Cl) is the target reaction product and the latter (H_2O) is the reaction byproduct). Figure 2 depicts the P-graph representations of these five reaction steps. The maximal reaction network in Figure 3 is generated from these P-graphs via algorithm MSG. Figures 4–6 exhibit 12 solution structures that correspond to combinatorially feasible reaction networks generated by algorithm SSG. The total computing time is <0.1 s on a 266 MHz Pentium personal computer (PC).

As indicated previously, the synthetic routes can be identified by ILP, subject to molar-balance constraints. Based on such constraints, the combinatorially feasible reaction networks **1**, **2**, and **3** in Figure 4, **6** and **7** in Figure 5, and **10** and **12** in Figure 6 are feasible; the remaining reaction networks are infeasible. Figures 4–6 also list the resultant overall reactions (R_{or}) of seven feasible reaction networks (i.e., alternative synthetic routes).

3.2. Assessment of Sustainability-Potential. The sustainability-potential of every alternative synthetic route is assessed based on its overall reaction for the manufacture of one unit of vinyl chloride (C_2H_3Cl). Table 1 lists the chemical exergies, unit prices, and toxicity indexes of the starting reactants and final reaction products of each synthetic route (i.e., the reacting species involved in each overall reaction).

3.2.1. Available Energy or Exergy Dissipation. The exergy dissipation of each alternative synthetic route is computed according to eq 1; the results are summarized in Table 2. Thus,

$$\overline{\Delta\epsilon_0} = -1971.93 \text{ kcal/g-mol} \quad (\text{from eq 2})$$

and

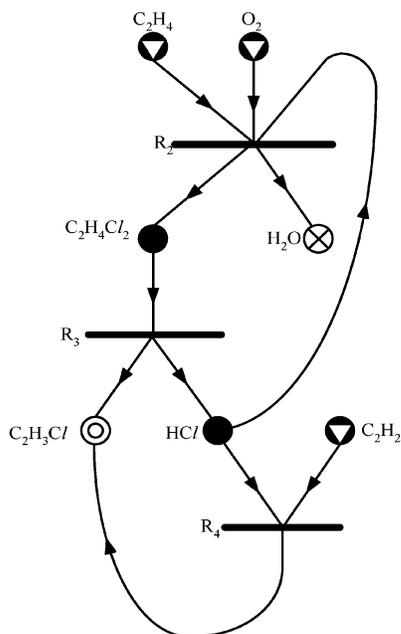
$$\sigma_{\Delta\epsilon_0} = 2532.91 \text{ kcal/g-mol} \quad (\text{from eq 3})$$

According to eq 4,

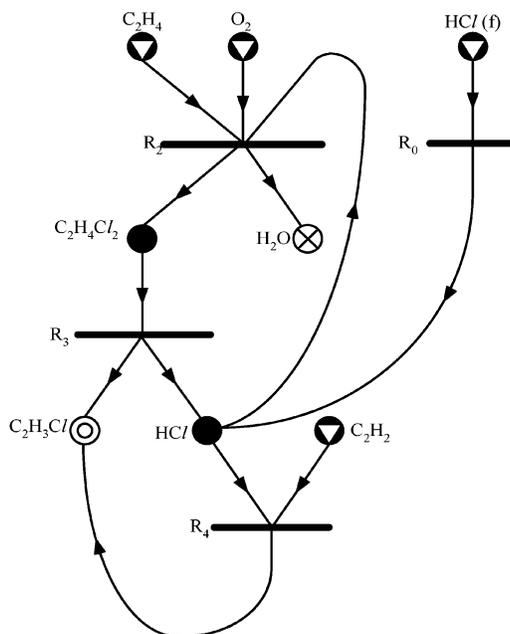
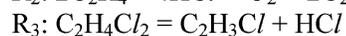
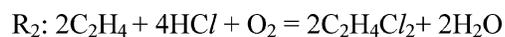
$$\begin{aligned} L_{\Delta\epsilon_0} &= \overline{\Delta\epsilon_0} - \sigma_{\Delta\epsilon_0} \\ &= (-1971.93 \text{ kcal/mol}) - (2532.91 \text{ kcal/mol}) \\ &= -4504.84 \text{ kcal/mol} \end{aligned}$$

Comparison of the $\Delta\epsilon_{0,i}$ values with $L_{\Delta\epsilon_0}$ indicates that $\Delta\epsilon_{0,1} > L_{\Delta\epsilon_0}$, $\Delta\epsilon_{0,2} > L_{\Delta\epsilon_0}$, $\Delta\epsilon_{0,3} > L_{\Delta\epsilon_0}$, $\Delta\epsilon_{0,6} > L_{\Delta\epsilon_0}$, $\Delta\epsilon_{0,7} > L_{\Delta\epsilon_0}$, $\Delta\epsilon_{0,12} > L_{\Delta\epsilon_0}$, and $\Delta\epsilon_{0,10} < L_{\Delta\epsilon_0}$. Hence, synthetic routes **1**, **2**, **3**, **6**, **7**, and **12** are acceptable, whereas synthetic route **10** is not, thereby eliminating it from the further consideration.

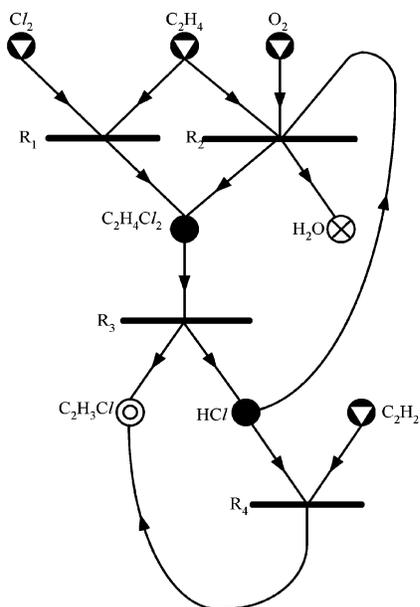
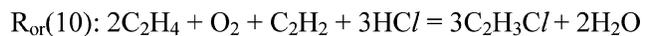
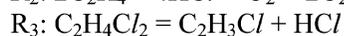
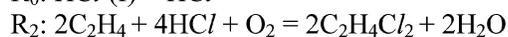
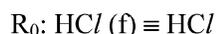
3.2.2. Potential Profit. The potential profits of synthetic routes **1**, **2**, **3**, **6**, **7**, and **12**, which have survived the scrutiny on the basis of available energy or exergy dissipation are computed according to eq 5; the results are also given in Table 2. The potential profits ($\Delta\zeta_i$) of synthetic routes **1**, **6**, **7**, and **12** are negative, whereas those of **2** and **3** are positive. Thus, only the last two are retained for further scrutiny, in regard to toxicity indices.



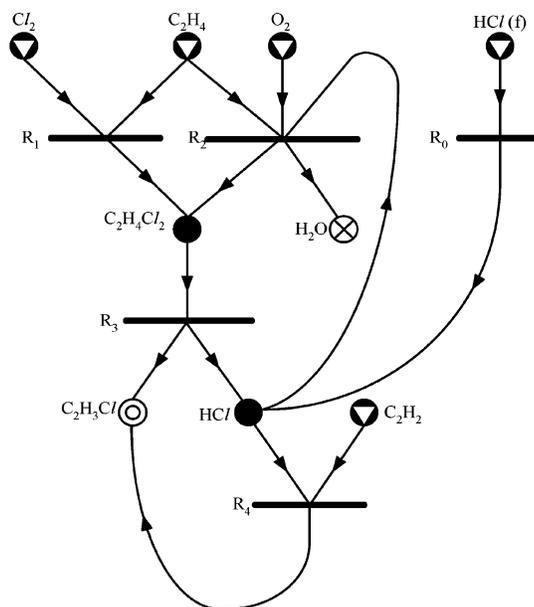
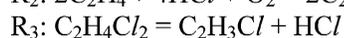
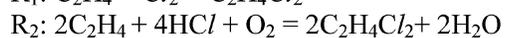
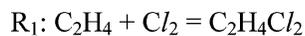
9



10



11



12

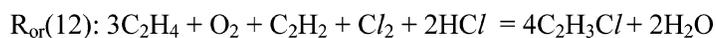
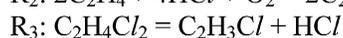
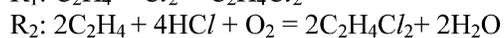
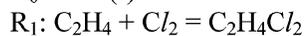
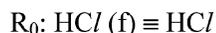


Figure 6. Combinatorially feasible reaction networks 9–12. Networks 10 and 11 are also feasible; note that HCl(f) can be simply replaced by HCl.

Table 2. Exergy Dissipation, Potential Profit, and Toxicity Index of the Overall Reaction of Each Alternative Synthetic Route for the Manufacture of a Single Unit of Vinyl Chloride (C₂H₃Cl)

synthetic route	overall reaction, R _{or}	exergy dissipation, Δε _{0,i} (kcal/g-mol)	potential profit, ΔC _i (¢/lb)	toxicity index, TID _i
1	C ₂ H ₂ + HCl = C ₂ H ₃ Cl	-1928.91	-32	
2	C ₂ H ₄ + Cl ₂ = C ₂ H ₃ Cl + HCl	1885.91	2.9	13
3	4C ₂ H ₄ + 2Cl ₂ + O ₂ = 4C ₂ H ₃ Cl + 2H ₂ O	-33.21	10.2	10.75
6	2C ₂ H ₄ + 2HCl + O ₂ = 2C ₂ H ₃ Cl + 2H ₂ O	-3904.27	-8	
7	C ₂ H ₄ + Cl ₂ + C ₂ H ₂ = 2C ₂ H ₃ Cl	-42.80	-45	
10	2C ₂ H ₄ + O ₂ + C ₂ H ₂ + 3HCl = 3C ₂ H ₃ Cl + 2H ₂ O	-5833.18		
12	3C ₂ H ₄ + O ₂ + C ₂ H ₂ + Cl ₂ + 2HCl = 4C ₂ H ₃ Cl + 2H ₂ O	-3947.07	-53	

3.2.3. Toxicity Indices. The toxicity indices of synthetic routes **2** and **3** are evaluated according to eq 7 and listed in Table 2. Thus,

$$\overline{\text{TID}} = 11.875 \quad (\text{from eq 7})$$

and

$$\sigma_{\text{TID}} = 1.125 \quad (\text{from eq 8})$$

According to eq 9,

$$\begin{aligned} L_{\text{TID}} &= \overline{\text{TID}} - \sigma_{\text{TID}} \\ &= 11.875 - 1.125 \\ &= 10.75 \end{aligned}$$

Comparison of the TID_i values with L_{TID} indicates that TID₂ > L_{TID} and TID₃ = L_{TID}. Thus, both synthetic routes **2** and **3** are acceptable, based on their toxicity indices.

4. Discussion

The efficacy of the proposed approach is demonstrated with the well-known example of manufacturing vinyl chloride (C₂H₃Cl).^{9,38-42} The combinatorial complexity of reaction-network synthesis, resulting in synthetic routes, is magnified exponentially with the number of reaction steps, *n*. When HCl serves as one of potential starting reactants in synthesizing C₂H₃Cl, *n* = 5, which includes the gate reaction, signifying the external supply of HCl. It would be indeed arduous and time-consuming to identify exhaustively the combinatorial feasible networks in (2⁵ - 1), or 31 possible reaction networks by resorting to any conventional algorithmic method for combinatorial analysis. Nevertheless, we have identified, at the outset, 12 combinatorially feasible synthetic routes in a fraction of a second on the aforementioned, moderately sized PC with algorithms MSG and SSG of the inordinately efficient graph-theoretic method based on P-graphs, whose effectiveness has been increasingly recognized.⁵⁰⁻⁵⁴ Moreover, these 12 combinatorially feasible synthetic routes have resulted in 7 feasible, or alternative, synthetic routes with ease via ILP.

Subsequently, the sustainability-potentials of the resultant alternative synthetic routes have been sequentially assessed in the order of their importance (i.e., hierarchically), in terms of the specified three criteria, including available energy (or exergy) dissipation, the potential profit, and the toxicity index, at the first, second, and third step, respectively. As a result, synthetic routes **2** and **3** have been determined to be potentially sustainable. Synthetic route **3**, which does not involve hydrogen chloride (HCl) either as a starting reactant or as a reaction byproduct, seems to be the synthetic route of choice in the industry worldwide.⁴² Nevertheless, synthetic route **2**, which yields HCl as the reaction byproduct, is still in use in Europe; this largely hinges on the marketability of HCl.⁹

Naturally, the alternative synthetic routes can be assessed further in regard to other criteria, such as the ecological and environmental impacts, societal concerns, and regulatory constraints, as they become sufficiently quantifiable. Nevertheless, the three criteria taken into account in the current work seem to suffice for rapid screening. Strictly speaking, the bounds of these three criteria can be made more stringent or less stringent, e.g., [-1/2σ] or (-2σ) instead of (-σ), for comparing exergy dissipation and toxicity index, and the minimum potential profit can be some positive value in place of zero. Moreover, the criteria can be evaluated by different formula for varied requirements or for a specific class of processes. It is worth noting that the first criterion estimated in regard to available energy (or exergy) dissipation has the most fundamental importance: The second-law (thermodynamic) analysis of any process, in terms of the available energy balance, entails an exhaustive account of the various material species and forms of energy involved and their transformation; in other words, it implicitly embodies mass and energy balances, which are essential for the assessment of sustainability.

Synthetic routes **2** and **3**, which have survived scrutiny, are tentatively deemed worthy of further development through pilot-scale experimentation and/or preliminary design (i.e., process synthesis). The sustainability of the processes emerging from such efforts should eventually be assessed via some of the available methods for sustainability analysis, which often entail the deployment of multiobjective optimization that considers all criteria simultaneously.⁵⁵⁻⁵⁸

Broadly speaking, process synthesis (i.e., process flowsheeting) based on the potentially sustainable synthetic routes that have been identified proceeds as follows.^{9,42} At the outset, a plausible class of chemical reactors or reacting units are assigned to each of the reaction steps. Every reacting unit is succeeded by a set of separation and/or mixing units. Collectively, they are the major operating units that must be taken into account in the synthesis, even though the mixing function often occurs in-line; therefore, customarily, the corresponding mixing units are not explicitly noted in the flowsheet.

A singular case is a biochemical process in which only a single reacting unit, specifically a fermentor, or fermenting unit, resides at the head of the process, which is usually followed by a sequence or sequences of separating and/or mixing units, thereby resulting in the notion of downstream processing.⁵⁹ Obviously, process synthesis entails composing the networks of all the major operating units assigned or identified, thus often leading to inordinate combinatorial complexity, similar to the reaction-network synthesis, but frequently even much more so, because of the substantial increase in the number of operating units involved.³²⁻³⁴

The profound complexity of process-network synthesis can be circumvented by deploying the graph-theoretic method based on P-graphs. For instance, our previous investigation of downstream process synthesis for biochemical production of butanol generated a set of technically feasible and cost-effective

flowsheets in the ranked order by this method.⁵⁹ Naturally, the potentially unsustainable flowsheets among them can be eliminated by resorting to the approach proposed in the current work.

A comprehensive procedure has been proposed recently by Gadewar et al.⁶⁰ for rapid process design. Such a procedure should be of particular interest in the present highly competitive economic environment. The procedure contains three phases, of which Phase 1 is identified to be the most crucial and is based on the discovery chemistry of the process. In light of the current intense focus on, and need for, assessing the sustainability of any industrial system or process, the usefulness of the proposed procedure for rapid process design would be substantially enhanced if the sustainability-potential of the process is estimated at the outset of Phase 1: The notion of sustainability-potential is also based mainly on the discovery chemistry of the process.

5. Concluding Remarks

A novel hierarchical approach has been proposed to estimate the sustainability-potential of a chemical process evolved from any of the alternative synthetic routes. The approach renders it possible to rapidly screen out processes that are highly unlikely to be sustainable, at the earliest possible stage, thereby preventing the enormous expenditure required for developing such processes. The proposed approach has been applied to an existing chemical process; the results have amply demonstrated its profound efficacy.

Supporting Information Available: Discussion of the dead or extended standard state, the derivation of the expressions for calculating partial molar enthalpy, entropy, and exergy, and reaction-network synthesis via the graph-theoretic method based on process graphs (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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