Life Cycle Sustainability Assessment of Chemical Processes: A Vector-based Three-dimensional Algorithm Coupled with AHP

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ABSTRACT: In this study, an integrated vector-based three-dimensional (3D) methodology for the life cycle sustainability assessment (LCSA) of chemical process alternatives is proposed. In the methodology, a 3D criteria assessment system is first established by using the life cycle assessment, the life cycle costing, and the social life cycle assessment to determine the criteria from the environmental, economic, and social pillars, respectively. The methodology incorporates the analytic hierarchy process (AHP) method to convert experts' judgments on the soft criteria into quantitative data and realize a unitary scale for both quantified soft criteria and normalized hard criteria. After assigning appropriate weights to each pillar and criterion by using the AHP method, the sustainability of the alternative processes can be prioritized by employing a novel vector-based algorithm, which combines the absolute sustainability performance and the relative sustainability deviation of the investigated processes. A case study on the sustainability assessment of three alternative ammonia production processes demonstrates that the proposed methodology is able to serve as a comprehensive and rigorous tool for the stakeholders to rank and identify the most sustainable chemical process alternatives.

Keywords: life cycle sustainability assessment, chemical process, analytic hierarchy process, vector-based algorithm.

1. INTRODUCTION

The chemical industry plays a significant role in the global development to meet the growing needs for chemicals and energies, however, the chemical production systems are deemed as processes with great investment and high energy consumption, and could cause severe environmental and social problems. Therefore, it is essential to incorporate the concept of sustainability into the chemical industry for achieving its healthful development. The central philosophy of sustainability is the triple-bottom-line balance, focusing on the simultaneous optimization of environmental impacts, economic prosperity, and social responsibility.[1] Accordingly, as a growing trend, the methodologies for the sustainability assessment of industry systems should be able to consider all the three pillars. Othman et al.[1] presented a methodology for assessing and selecting the most sustainable chemical process through embedding the economic-environment-social criteria in the analytic hierarchy process (AHP) method. Hoffmann et al.[2] introduced a new approach for evaluating multiple process alternatives while taking explicit account of uncertainties, offering a promising way to address the multiobjective design problems for chemical industry at the early stages. Luo et al.[3] developed a set of emergy-based sustainability indices to assess the economic, environmental, and eventually sustainability status of an industry system. An interval-parameter-programming-based strategic planning method for investigating the industrial production sustainability issues was proposed by Liu and Huang[4] to involve a set of sustainability metrics from all the environmental, economic, and social aspects. Moradi-Aliabadi and Huang[5] introduced a three-dimensional algorithm to reflect the sustainable development potential of an industrial process, in which, a 3D sustainability was defined to quantify the balance of triple-bottom-line-based development, providing a mathematical method for formulating sustainability problems as a general vector-based analysis problem. A framework for optimal process sustainability performance enhancement was established while taking into account of uncertainties and dealing data uncertainty by using interval parameters; the framework can be adopted in the sustainability optimization problems with different objective functions.[6] A multicriteria decision-making (MCDM) methodology was developed by Ren et al.[7] for the sustainability assessment and prioritization of industrial systems by incorporating the fuzzy AHP and fuzzy analytic network process (ANP) methods; the methodology can not only consider both the quantitative and qualitative criteria from all the environmental, economic, and social dimensions, but also handle the interdependencies and interactions between these criteria. Serna et al.[8] also proposed a multicriteria analysis based framework to prioritize multiple chemical processes with sustainability criteria, where the relative importance of criteria were determined by AHP, and the influences between economic, environmental, safety and health criteria groups were addressed by the Decision Making Trial and Evaluation Laboratory (DEMATEL) technique.

Recently, the life cycle sustainability assessment (LCSA) as an emerging method for addressing the sustainability performance of alternative systems from a life cycle perspective, has received more and more attentions. The LCSA method is essentially the integration of three life cycle techniques - Life Cycle Assessment (LCA) for environmental performance, Life Cycle Costing (LCC) for economic issues, and Social Life Cycle Assessment (S-LCA) for social concerns, which can be represented as LCSA=LCA+LCC+S-LCA.[9] Taking LCSA as a powerful tool, multiple practices have been attempted to assess and prioritize the sustainability of systems like biodiesel manufacture,[10] concrete recycling,[11] polycrystalline silicon production,[12] and alternative fertilizers.[13] Meanwhile, a variety of studies have also been carried out to improve the LCSA method and extend its applications. Kloepffer[14] provided guidelines for incorporating LCA, LCC, and S-LCA into LCSA, offering a way to balance the three pillars in sustainability assessment. A LCSA framework was suggested by Guinee et al.[15] for linking life cycle sustainability questions to knowledge for addressing them, identifying available knowledge and related models, knowledge gaps, and defining research programs to fill these gaps. Halog and Manik[16] proposed an integrated methodology to combine the multi-criteria decision analysis and dynamic system modeling with the LCSA method for sustainability assessment. Pesonen and Horn[17] developed a streamlined LCSA assessment tool -"Sustainability SWOT"- for drafting sustainable strategies rapidly and cost-efficiently. Ren et al.[18] developed a mathematical methodology for sustainability assessment by combining the LCSA framework with two multi-criteria decision-making models, i.e. the Vlsekriterijumska Optimizacija I Kompromisno Resenje (VIKOR) method and the AHP method. For addressing the problem of sustainable chemical engineering, Azapagic and Perdan[19] argued that the best way is adopting a systems methodology and considering simultaneously all three economic, environmental and social pillars on a life cycle basis.

Despite the emergence and development of the LCSA method in the sustainability assessment of industry systems, its application in chemical processes is still in the infant stage due to a couple of critical issues: (1) the life cycle sustainability assessment of chemical processes usually involves soft criteria that are difficult or impossible to be quantified and can only be described qualitatively. Therefore, an effective LCSA methodology for the sustainability assessment of chemical processes should be able to handle both the hard and soft criteria. (2) The sustainability assessment and prioritization of the alternative chemical processes are typical multiple-criteria decision problems, which have to consider the criteria with respect to all the three sustainability pillars, i.e. the environmental impacts, economic prosperity and social responsibility, and resolve the trade-offs between them. Accordingly, it is of vital importance to develop an integrated three-dimensional method that is capable of determining the sustainability performance of each alternative with respect to the three pillars.

In a previous report by Moradi-Aliabadi and Huang,[5] a 3D vector function based on the concept of “triple-bottom-line” was defined to evaluate the sustainability status of a industry system, providing a promising method to analyze the sustainability improvement process of industry systems by applying vector-based techniques. In the method, any system’s “transition toward sustainability” can be represented by the length and direction of a vector. Inspirited by this work,[5] a vector-based 3D methodology for the sustainability assessment of chemical processes by combining the LCSA method with the AHP method and a vector-based algorithm was developed in this study. In the methodology, the performance of each alternative with respect to the soft criteria, as well as the relative weights of the pillars and criteria were quantified by using the AHP method, which allows the decision-makers to assess them using qualitative description. Subsequently, a novel vector-based algorithm was proposed to prioritize the sustainability performance of the alternative processes by incorporating the magnitude and direction of a 3D vector into a normalized vector projection. During which, the magnitude of the vector was calculated to score the absolute sustainability performance of the alternative chemical processes, the angle was used to quantify the relative deviation of their sustainability performance from the totally sustainable direction, while the projection value can inform the decision-makers a more comprehensive and rigorous sustainability assessment result by combining the magnitude and direction.

The remainder of this paper is organized as follows: Section 2 introduces the mathematical framework; Section 3 presents a case study to assess and prioritize the sustainability of three alternative ammonia production processes for illustrating the developed methodology; Section 4 offers the results comparison; Section 5 gives the study's discussions and conclusions.

2. MATHEMATICAL FRAMEWORK

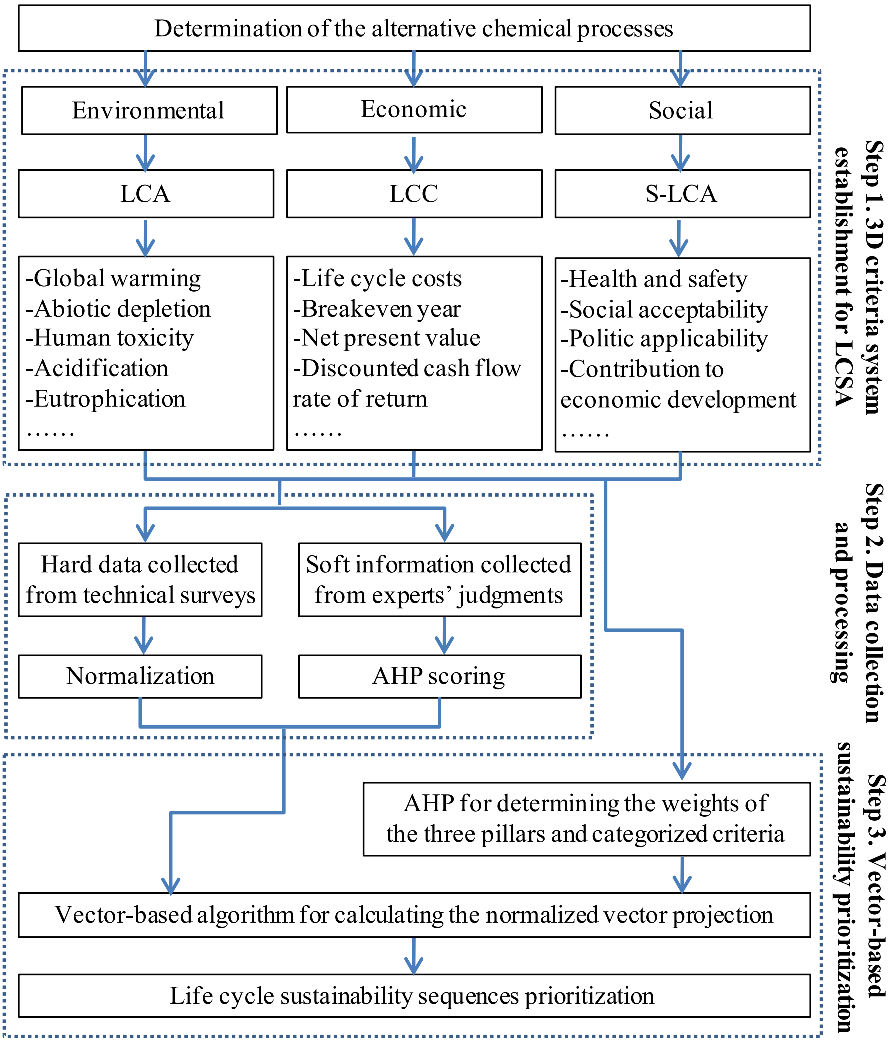

Figure 1. Framework of the proposed LCSA method for chemical processes.

The framework of the proposed mathematical methodology is illustrated in Figure. 1, which includes three steps. In the first step, the 3D criteria system for the life cycle sustainability assessment is established, in which, the LCA, LCC, and S-LCA methods are, respectively, used to determine the criteria from the environmental, economic, and social pillars. In the second step, the data and information of the alternatives with respect to both the hard and soft criteria are collected, subsequently, the data of hard criteria collected from the technical surveys with different units and scales are normalized into a dimensionless and unitary scale, while the qualitative information of soft criteria provided by the experts are converted into quantitative values by using the AHP method. In the third step, the sustainability performance of the chemical processes is prioritized by combining the developed vector-based algorithm with the AHP method. During the process, the weight of each pillar and criterion is determined by using the AHP method according to their relative importance, the sustainability performance regarding each alternative is then expressed as a 3D vector function, which was used to compare the sustainability of different alternatives by integrating the absolute sustainability performance (the vector's magnitude) and the relative sustainability deviation (the vector's direction).

2.1 Establishment of the 3D Criteria System

2.1.1 Criteria Identification in the Environmental Dimension by LCA

LCA is essentially a "cradle to grave" method to identify the environmental criteria for the sustainability assessment. Due to the growth of environmental awareness over the last decades, a variety of criteria concerning the environmental impacts can be obtained by utilizing several well-developed LCA methodologies, such as CML 2001, EDIP 2003, Eco-Indicator 99, and Impact 2002+, etc. In general, these methodologies provide three categories of criteria for evaluating the environmental sustainability, i.e. human health, ecosystem quality, and recourses consumption. For example, ten categories are included in CML 2 baseline 2000 V2.04 characterization: abiotic depletion, acidification, eutrophication, global warming, ozone layer depletion, human toxicity, fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, and photochemical oxidation.[20] As for the chemical processes, other important criteria like the ratio of water withdrawal-to-availability,[21] as well as energy efficiency and exergy efficiency[22] could also be taken into the consideration according to the actual conditions.

2.1.2 Criteria Identification in the Economic Dimension by LCC

By following the same logic of "from birth to death", the total cost of the product over its entire life stages including the processes of design, development, use and disposal can be assessed by using the LCC method.[23] For implementing LCC, several routes such as analogy model, parametric model, and engineering cost model can be utilized, in which, the costs for investment, operation, maintenance, and feedstock are usually integrated into the total cost, while the decommissioning and recycling costs are also frequently accounted.[24] For the chemical processes, indicators such as breakeven year,[25] net present value, and discounted cash flow rate of return,[1] can also be included.

2.1.3 Criteria Identification in the Social Dimension by S-LCA

For addressing the social impacts of the alternatives, a wide range of evaluation indicators "from direct impacts on workers to broader societal consequences" have been integrated into the life cycle sustainability assessment.[26] For example, according to the UNEP/SETAC guidelines,[27] worker, consumer, local community, society, and value chain actors are considered as the stakeholder categories, which include 31 subcategories like health and safety, local employment, contribution to the economic development, etc. Since the development of S-LCA has just experienced a short history,[28] the decision-makers can choose appropriate methodology and suitable criteria according to the actual circumstance and their preferences.

2.2 Data Collection and Processing

The criteria in the established 3D system indentified by life cycle techniques can be divided into two types: hard and soft.[1] The hard criteria belong to the objective indicators that can be assessed quantitatively using crisp numbers, while the soft ones are subjective measures which depend on the qualitative evaluation deprived from the decision-makers' knowledge and experience. Therefore, two different routes for data and information collection and processing were used for the hard and soft criteria, respectively.

2.2.1 Data Collection and Normalization for the Hard Criteria

The hard criteria refer to the factors that can be quantitatively evaluated by adopting crisp numbers, e.g. the criteria of global warming and human toxicity identified by the LCA method,[22] the criterion of life cycle costs[29] established by the LCC method, and even the criterion of inherent safety[30] in the social aspect. Herein, serious technique surveys are needed for collecting accurate data regarding the alternative processes with respect to each hard criterion, which may rely on different literature source, system simulations, and mathematical techniques.[4] For chemical processes, one can obtain the corresponding information by process simulation using the well-established commercial packages like Aspen Plus.[4, 31] Subsequently, the simulation information regarding the environmental and techno-economic performance can be utilized for generating the hard data regading the criteria, during which, the LCA database such as SimaPro could be combined into the simulation process for better understanding the enivironmental performance.[22]

Since the collected quantitative data have different physical units and scales, it is prerequisite for the sustainability assessment to normalize the values of all the criteria into dimensionless and unitary data. In this study, Eq 1 is employed to normalize the benefit criteria (the priority of the corresponding alternative increases with an increase in the value of the benefit criteria) or the cost criteria (the priority of the corresponding alternative decreases with an increase in the value of the cost criteria), respectively.[32]

$$\begin{aligned} &\text{Benefit}: r_k(i) = \frac{x_k(i)}{\sqrt{\sum_{i=1}^{N} x_k(i)^2}} \\ &\text{Cost}: r_k(i) = 1 - \frac{x_k(i)}{\sqrt{\sum_{i=1}^{N} x_k(i)^2}} \end{aligned} \tag{1}$$

where $x_k(i)$ is the collected data regarding the *i*-th alternative with respect to the *k*-th hard criterion, while $r_k(i)$ as the normalized data from 0 to 1, indicating the performance of the *i*-th alternative with respect to the *k*-th hard criterion.

2.2.2 Information Collection and Scoring for the Soft Criteria

In contrary to the hard criteria, the soft criteria can only be described by subjective measures that depend heavily on the involved decision-makers' knowledge and experience. The soft criteria are commonly found in the social aspect, e.g. social acceptability and policy applicability.[18] For collecting reasonable and reliable information, the experts with professional insights are recommended to contribute their qualitative judgments on the relative priorities of the alternatives with respect to each soft criterion, which is usually by two ways: the scaling system method[33] and the pairwise comparison method.[34, 35] The scaling method scores the relative priorities by using numbers, which is simple and easy to be operated by the users; however, it cannot assure the overall consistency among all the relative priorities.[7] The pairwise comparison method is to determine the relative priorities of the alternatives through pairwise comparison, offering a more reliable scoring result with consistency.[34] In this study, the AHP approach, one of the most famous pairwise comparison methods, was adopted for scoring the experts' qualitative description on the soft criteria via the following procedures.[34, 35]

Step 1: Establishing the comparison matrix. The involved experts are required to establish the comparison matrix (eq 2) by using Satty's 1-9 scale (Table 1).

Table 1. The qualitative description and the corresponding numerical scale of the relative priority used in the comparison matrix[34]

numerical Scale	definition
1	equal importance
3	moderate importance
5	essential importance
7	very strong importance
9	absolute importance
2,4,6,8	intermediate value
reciprocal	Reciprocals of above

$$\begin{bmatrix} y_k(11) & y_k(12) & \cdots & y_k(1N) \\ y_k(21) & y_k(22) & \cdots & y_k(2N) \\ \vdots & \cdots & \ddots & \cdots \\ y_k(N1) & y_k(N2) & \cdots & y_k(NN) \end{bmatrix} \tag{2}$$

where $y_k(ij)$ refers to the converged judgment of the experts regarding the *i*-th alternative compared to the *j*-th alternative with respect to a given soft criteria *k*.

Step 2: Calculating the maximum eigenvector and the maximum eigenvalue. By running eq3, the maximum eigenvector $(p_k(1), p_k(2), \cdots, p_k(N))^T$ and the maximum eigenvalue $\lambda_{\max}$ of the comparison matrix can be computed. Subsequently, eq 4 is used to normalize the elements in the maximum eigenvector.

$$\begin{bmatrix} y_k(11) & y_k(12) & \cdots & y_k(1N) \\ y_k(21) & y_k(22) & \cdots & y_k(2N) \\ \vdots & \cdots & \ddots & \cdots \\ y_k(N1) & y_k(N2) & \cdots & y_k(NN) \end{bmatrix} \begin{bmatrix} p_k(1) \\ p_k(2) \\ \vdots \\ p_k(N) \end{bmatrix} = \lambda_{\max} \begin{bmatrix} p_k(1) \\ p_k(2) \\ \vdots \\ p_k(N) \end{bmatrix} \tag{3}$$

$$\bar{P}_k(i) = \frac{p_k(i)}{\sum_{i=1}^{N} p_k(i)} \tag{4}$$

Step 3: Checking the consistency of the comparison matrix. The consistency of the comparison matrix is firstly measured using the consistency index (*CI*) as shown in eq 5, then, the consistency ratio (*CR*) is calculated by Eq 6 for judging whether a comparison matrix is acceptable. If $CR \geq 0.1$, the comparison matrix has to be revised.

$$CI = \frac{(\lambda_{\max} - NP)}{(NP - 1)} \tag{5}$$

$$CR = \frac{CI}{RI} \tag{6}$$

In eq 5, *NP* denotes the number of parameters; in eq 6, *RI* is the random index that can be checked in Table S1. Notably, once a comparison matrix is acceptable, the normalized element $\overline{P}_k(i)$ in eq 4 with uniform distribution from 0 to 1 is used to represent the scored performance of the *i*-th alternative regarding the soft criterion *k*.

2.3. Vector-based Sustainability Prioritization

2.3.1. Weights Determination for Pillars and Criteria

When evaluating the sustainability performance of a chemical process, the relative weight of each pillar and criterion needs to be firstly determined. In real-world issues, the weights of the three pillars are usually unequal, indicating that the more favored pillar has more influence on the overall sustainability performance. Similarly, it is necessary to assign the relative weight to each categorized criterion based on the importance of each criterion to the sustainability performance of the corresponding pillar. Herein, the AHP method was employed again to determine the weight based on the pairwise comparison of one pillar (or categorized criterion) over another.

2.3.2 Vector-based Algorithm

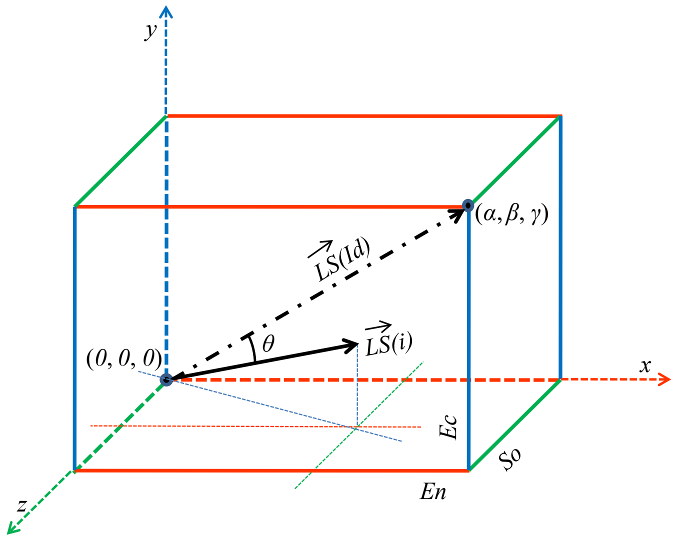

Figure 2. The principal of a triple-bottom-line-based 3D vector space.

The complete sustainability assessment of a chemical process can be expressed as a vector in the triple-bottom-line-based 3D space as shown in Figure. 2, which is developed based-on the literatures;[5, 31, 36] in which, *α*, *β,* and *γ* are the relative weights associated with the environmental, economic, and social pillar, respectively. Geometrically, the sustainability of a chemical process is presented by the vector of $\overrightarrow{LS}(i)$ (eq 7) with the vector tail (0, 0, 0) referring to "no sustainability"; while the highest sustainability that the chemical process can ideally achieve is indicated by the ideal vector of $\overrightarrow{LS}(Id)$ (eq 8) with the corner (*α*, *β*, *γ*) indicating "complete sustainability".[5, 31] Obviously, one can judge the sustainability performance of the chemical process by two factors, that is, the magnitude of the $\overrightarrow{LS}(i)$ vector (eq 9), demonstrating the absolute sustainability performance, and the deviation of $\overrightarrow{LS}(i)$ from $\overrightarrow{LS}(Id)$ (eq10), presenting the deviation of the sustainability performance from the totally sustainable direction.

$$\overrightarrow{LS}(i) = \langle \alpha En(i), \beta Ec(i), \gamma So(i) \rangle = \alpha En(i)\hat{x} + \beta Ec(i)\hat{y} + \gamma So(i)\hat{z} \tag{7}$$

$$\overrightarrow{LS}(Id) = \langle \alpha, \beta, \gamma \rangle = \alpha\hat{x} + \beta\hat{y} + \gamma\hat{z} \tag{8}$$

$$\left\| \overrightarrow{LS}(i) \right\| = \sqrt{\alpha^2 En^2(i) + \beta^2 Ec^2(i) + \gamma^2 So^2(i)} \tag{9}$$

$$\theta(\overrightarrow{LS}(i)) = \arccos\left(\frac{\overrightarrow{LS}(i) \cdot \overrightarrow{LS}(Id)}{\left\|\overrightarrow{LS}(i)\right\| \left\|\overrightarrow{LS}(Id)\right\|} \right) \tag{10}$$

In eq 7, $\hat{x}$, $\hat{y}$, and $\hat{z}$ are the standard unit vectors in the three directions, $En(i)$, $Ec(i)$, and $So(i)$ are the quantified composite performances of a process i with respect to the three pillars, which are defined by eqs.11-13.[4, 31]

$$En(i) = \sum_{k=1}^{u} a_k En_k(i) \tag{11}$$

$$Ec(i) = \sum_{k=1}^{v} b_k Ec_k(i) \tag{12}$$

$$So(i) = \sum_{k=1}^{w} c_k So_k(i) \tag{13}$$

where a_k, b_k, and c_k represent the weights assigned to the k-th criterion in the corresponding pillar, $En_k(i)$, $Ec_k(i)$, and $So_k(i)$ are the processed data of the i-th alternative regarding to the k-th criterion, u, v, and w represent the criteria number in each pillar.

The absolute sustainability performance (the vector's magnitude) offers a triple-bottom-line-based sustainability score by resorting to the vector magnitude concept, performing a similar sustainability assessment as many MCDM approaches do, which require the same information of weight and performance for each criterion that can then be assembled in a unique synthesizing score by the widely applied additive and multiplicative aggregations.[37] While the relative sustainability deviation (the vector's direction) measures the relative deviation of the investigated process compared to the ideal sustainability direction, highlighting that a satisfactory process should balance the environmental, economic, and social sustainability, simultaneously. Therefore, the direction indicator can be used to identify the unsatisfactory alternatives that perform excessively bad in any pillar but good in the other pillars. As shown in Figure. 3, a process can be regarded as a more sustainable route when the corresponding vector has a larger magnitude and a smaller deviation from the ideal vector, e.g. P_1 versus P_3. However, a decision-making confusion may arise when a process acts better in the magnitude but worse in the direction (such as P_1 compares to P_2), and vice versa. For this reason, the normalized projection of each vector on the ideal vector $P_{Id}\overrightarrow{LS}(i)$ (eq 15) is proposed in this study to measure the ultimate sustainability performance of the alternative processes by incorporating both the magnitude and direction of the investigated vector. Apparently, the projection value of each vector lies between 0 and 1 by deeming that the projection of the ideal vector is equal to 1 (eq 14). For convenience, Fig. 3 illustrated the relationship between $\overrightarrow{LS}(i)$, $\theta(\overrightarrow{LS}(i))$, and $P_{Id}\overrightarrow{LS}(i)$ in a 2D view.

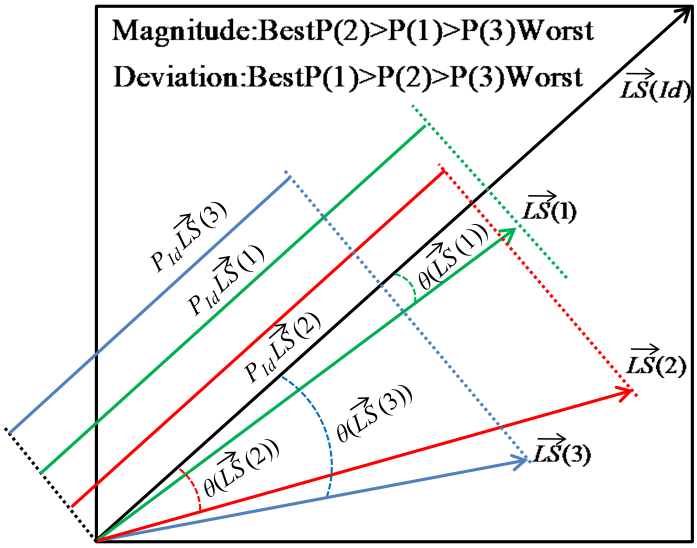

Figure 3. The relationship between $\overrightarrow{LS}(i)$, $\theta(\overrightarrow{LS}(i))$, and $P_{Id}\overrightarrow{LS}(i)$.

$$P_{Id}\overrightarrow{LS}(Id) = \frac{\left\|\overrightarrow{LS}(Id)\right\|\cos\theta(\overrightarrow{LS}(Id))}{\sqrt{\alpha^2+\beta^2+\gamma^2}} = \frac{\sqrt{\alpha^2+\beta^2+\gamma^2}\times\cos\theta(0)}{\sqrt{\alpha^2+\beta^2+\gamma^2}} = 1 \tag{14}$$

$$P_{Id}\overrightarrow{LS}(i) = \frac{\left\|\overrightarrow{LS}(i)\right\|\cos\theta(\overrightarrow{LS}(i))}{\sqrt{\alpha^2+\beta^2+\gamma^2}} = \frac{\left\|\overrightarrow{LS}(i)\right\|\left(\frac{\overrightarrow{LS}(i)\cdot\overrightarrow{LS}(Id)}{\left\|\overrightarrow{LS}(i)\right\|\left\|\overrightarrow{LS}(Id)\right\|}\right)}{\left\|\overrightarrow{LS}(Id)\right\|}$$
$$= \frac{\overrightarrow{LS}(i)\cdot\overrightarrow{LS}(Id)}{(\left\|\overrightarrow{LS}(Id)\right\|)^2} = \frac{\alpha^2 En(i)+\beta^2 Ec(i)+\gamma^2 So(i)}{\alpha^2+\beta^2+\gamma^2} \tag{15}$$

3. CASE STUDY

For illustrating the proposed method, the life cycle sustainability of three alternative ammonia production processes, including one conventional route of coal-syngas-ammonia (CSA) and two promising pathways of nuclear-hydrogen-ammonia (NHA) and hydropower-hydrogen-ammonia (HHA), was assessed and prioritized. The detailed information regarding each process can be found in the literature.[22]

CSA Process

A typical CSA process of a coal-based ammonia plant with CO_2 sequestration technology was showed in Fig. 4.[38] The first unit of the process is coal gasification, including the stages of desulfurization, reforming (with steam or/and oxygen), water–gas shift, and purification, with the aim to produce syngas (H_2 and CO). The second unit of the process is ammonia synthesis, which relies on the Haber-Bosch (HB) synthesis loop to convert the mixture of hydrogen and nitrogen into ammonia. In CSA process, electrical energy has to be input for CO_2 sequestration and ammonia synthesis.

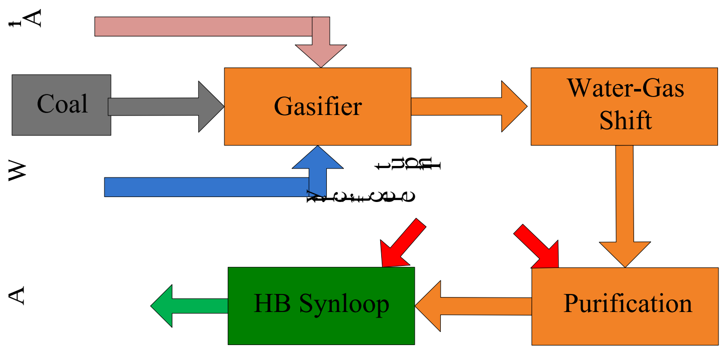

Figure 4. The diagram of CSA process.

NHA Process

In the NHA process (Figure. 5),[22] a high-efficiency nuclear plant is employed to provide electricity for the units of HB ammonia synthesis and cryogenic air separation (CAS) for producing nitrogen, while the nuclear waste heat is supplied to a high temperature electrolysis (HTE) plant for hydrogen generation.

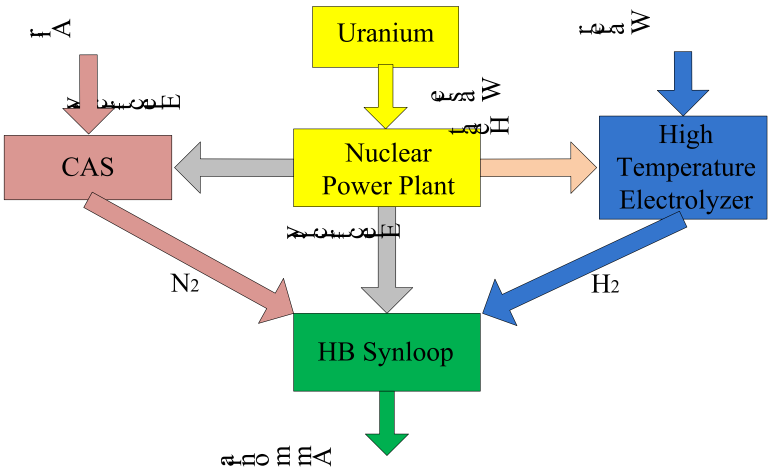

Figure 5. The diagram of NHA process.

HHA Process

In the HHA process (Figre.6),[22] a hydropower plant is used to produce electricity for the units of electrolysis, cryogenic air separation and the HB ammonia synthesis.

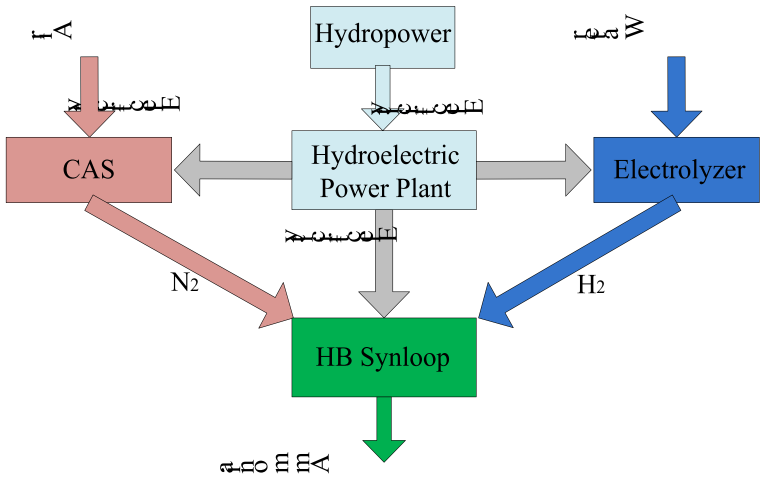

Figure 6. The diagram of HHA process.

In this case study, a total of seven criteria are taken into consideration (Table 2), including three environmental criteria obtained by LCA, i.e. global warming, abiotic depletion, and energy efficiency, one criterion in the economic aspect acquired by LCC, i.e. life cycle costs, three social performance identified by S-LCA, i.e.

contribute to economic development, social acceptability, and politic applicability. Among them, the data corresponding to the four hard criteria (Table 2) were obtained or deduced from technique surveys; while the information attributed to the three soft criteria were collected from the experts' judgments.

Table 2. LCSA Criteria for the alternative ammonia production processes

Pillars	Criteria	Type	Abbreviation
Environmental	Global warming	Hard (Cost)	En_1
	Abiotic depletion	Hard (Cost)	En_2
	Energy efficiency	Hard (Benefit)	En_3
Economic	Life cycle costs	Hard(Cost)	Ec_1
Social	Contribute to economic development	Soft	So_1
	Social acceptability	Soft	So_2
	Politic applicability	Soft	So_3

Environmental criteria

All the three environmental criteria belong to the hard type, in which, the cost criteria of global warming (En_1) and abiotic depletion (En_2), as well as the benefit criterion of energy efficiency (En_3) should be normalized by Eq 1. The data for the environmental criteria are presented in Table 3.

Table 3. Data for the environmental criteria

Criteria	Original Data			Normalized Data		
	En_1 ($kgCO_2$-eq)	En_2 (kgSb-eq)	En_3(LHV)	En_1	En_2	En_3
CSA	2.72 [39]	0.0027 [15]	43.4% [a]	0.0529	0.6413	0.6639
NHA	0.84 [15]	0.0064 [15]	23.8% [15]	0.7075	0.1498	0.3641
HHA	0.38 [15]	0.0029 [15]	42.7% [15]	0.8677	0.6147	0.6532

[a] The overall energy efficiency (LHV) for CSA (43.4%) is deduced from the LHV energy efficiency[40] of coal-to-syngas (gasification) process and the LHV energy efficiency[38] of the syngas-to-ammonia (synthesis) process.

Economic criterion

Life cycle costs (LCC) is the single criterion in the economic pillar, referring to the overall costs in all the stages of the alternative ammonia production processes, which can be calculated by eq16.

$$LCC = \frac{CC_{H_2} + CC_{N_2} + CC_{NH_3} + O\&M_{H_2} + O\&M_{N_2} + O\&M_{NH_3}}{Plant\ size} \quad (16)$$

where CC_{H_2}, CC_{N_2}, CC_{NH_3} are the capital costs of the units of hydrogen production, nitrogen generation and ammonia synthesis, respectively, including the costs of land, equipment, transportation and construction. $O\&M_{H_2}$, $O\&M_{N_2}$, and $O\&M_{NH_3}$ refer to the operation and maintenance costs of each unit.

The criterion of life cycle costs (Ec_1) belongs to the hard (cost) type, the corresponding data with respect to the three alternatives are presented in Table 4.

Table 4. Data of the economic pillar

Ec_1	Plant size	Capital costs (M$)			O&M costs (M$)			LCC	Normalized
	(t-NH_3/day)	CC_{H_2}	CC_{N_2}	CC_{NH_3}	$O\&M_{H_2}$	$O\&M_{N_2}$	$O\&M_{NH_3}$	$/(t-$NH_3$/day)	Data
CSA	1629[b]	691.4[31]	-[c]	200.4[c]	75.6[31]	-[c]	8.0[c]	599×10^3	0.5966
NHA	4318[b]	988.8[31]	290.3[c]	385.0[c]	586.7[31]	11.6[c]	15.4[c]	528×10^3	0.6445
HHA	300[b]	251.3[41]	50.7[c]	67.1[c]	1.6[41]	2.0[c]	2.7[c]	1251×10^3	0.1569

[b] Plant size for three ammonia synthesis processes are deduced from respective hydrogen plant studies;[38, 40]

[c] Capital costs and O&M costs for N_2 and NH_3 units are calculated based on the literature[38]; - refers that the capital cost and O&M cost for N_2 unit in CSA process are included in H_2 unit.

Social criteria

All criteria in the social pillar are the soft. Therefore, the AHP method is used for scoring the three criteria with respect to each process by incorporating the experts' judgments via the comparison matrixes as presented in Table5，6 and 7. Taking the cell (3,1) in Table 5 as an example, when comparing the process of HHA with CSA regarding the performance of "contribute to economic development (So_1)", the decision-makers have determined that HHA acts moderately better than CSA; thus, the corresponding pairwise comparison value is assumed to be 3. After gathering all the needed comparisons for So_1, by running eq 3, the maximum eigenvalue ($\lambda_{\max}$) can be calculated to be 3.0385 with the corresponding maximum eigenvector of $(0.1506, 0.9161, 0.3715)^T$. Then, the priority of the three alternatives with respect to So_1 can be scored to be $\overline{P}_{So_1} = (0.1047, 0.6370, 0.2583)^T$ after normalization according toeq 4. Finally, the consistency of the comparison matrix was checked, the *CI*) and *CR* were calculated to be 0.0193 and 0.032 according to eq 5 and eq 6, respectively. Since *CR*< 0.1, the matrix is regarded as "acceptable".

Table 5. Comparison matrix for scoring the soft criterion So_1

So_1	CSA	NHA	HHA	Scored Data
CSA	1	1/5	1/3	0.1047
NHA	5	1	3	0.6370
HHA	3	1/3	1	0.2583

$\lambda_{\max}$=3.0385 CI=0.0193 CR=0.0332 < 0.1

Table 6. Comparison matrix for scoring the soft criterion So_2

So_2	CSA	NHA	HHA	Scored Data
CSA	1	3	1/5	0.1884
NHA	1/3	1	1/7	0.0810
HHA	5	7	1	0.7306

$\lambda_{\max}$=3.0649 CI=0.0325 CR=0.0559 < 0.1

Table 7. Comparison matrix for scoring the soft criterion So_3

So_3	CSA	NHA	HHA	Scored Data
CSA	1	1/3	1/5	0.1047
NHA	3	1	1/3	0.2583
HHA	5	3	1	0.6370

$\lambda_{\max}$=3.0385 CI=0.0193 CR=0.0332 < 0.1

After the data or information of the three alternative processes with respect to the criteria were scored, their sustainability performance was then prioritized according to the vector analysis techniques. Firstly, the relative weights of the three pillars (*α*, *β,* and *γ*) were determined using the AHP method according to the comparison matrix (Table. 8), while the local weights a_k and c_k in eq 11 and eq 13 were also acquired via the AHP method (Table. 9 and Table. 10). Since there is only one criterion (life cycle costs) in the economic pillar, the local weight of the criterion (b_1 in eq 12) is equal to 1. Subsequently, the composite performances of the alternative processes with respect to the three pillars were calculated by eqs. 11-13, the normalized vector projection algorithm was then employed to obtain the ultimate sustainability performance of each process. Here, the calculating procedure for the CSA process was illustrated in eqs. 17–25 as an example, and the obtained assessment results for the three alternatives were presented in Table 11.

Table 8. Comparison matrix for determining the weights of the three pillars

	En	*Ec*	*So*	Coefficients
En	1	2	2	0.5000 (α)
Ec	1/2	1	1	0.2500 (β)
So	1/2	1	1	0.2500 (γ)
λ_{max}=3.000 CI=CR=0.0000 < 0.1				

Table 9. Comparison matrix for determining the weights of the three criteria in the environmental pillar

	En_1	En_2	En_3	Coefficients
En_1	1	3	5	0.6370 (a_1)
En_2	1/3	1	3	0.2583 (a_2)
En_3	1/5	1/3	1	0.1047 (a_3)
λ_{max}=3.085 CI=0.0193 CR=0.0332 < 0.1				

Table 10. Comparison matrix for determining the weights of the three criteria in the social pillar

	So_1	So_2	So_3	Coefficients
So_1	1	1/3	1	0.2000 (c_1)
So_2	3	1	3	0.6000 (c_2)
So_3	1	1/3	1	0.2000 (c_3)
λ_{max}=3.000 CI=CR=0.0000 < 0.1				

$$En(CSA) = \sum_{k=1}^{3} a_k En_k(CSA) = 0.2688 \tag{17}$$

$$Ec(CSA) = \sum_{k=1}^{1} b_k Ec_k(CSA) = 0.5966 \tag{18}$$

$$So(CSA) = \sum_{k=1}^{3} c_k So_k(CSA) = 0.1549 \tag{19}$$

$$\overrightarrow{LS}(Id) = 0.5\hat{x} + 0.25\hat{y} + 0.25\hat{z} \tag{20}$$

$$\overrightarrow{LS}(CAS) = 0.1344\hat{x} + 0.1492\hat{y} + 0.0387\hat{z} \tag{21}$$

$$\left\|\overrightarrow{LS}(Id)\right\| = \sqrt{\alpha^2 + \beta^2 + \gamma^2} = 0.6124 \tag{22}$$

$$\left\|\overrightarrow{LS}(CSA)\right\| = \sqrt{\alpha^2 En^2(CSA) + \beta^2 Ec^2(CSA) + \gamma^2 So^2(CSA)} = 0.2045 \tag{23}$$

$$\theta(\overrightarrow{LS}(CSA)) = \arccos\left(\frac{\overrightarrow{LS}(CSA)\cdot\overrightarrow{LS}(Id)}{\left\|\overrightarrow{LS}(CSA)\right\|\left\|\overrightarrow{LS}(Id)\right\|}\right)$$
$$= \arccos\left(\frac{0.1344\times 0.5 + 0.1492\times 0.25 + 0.0387\times 0.25}{0.2045\times 0.6124}\right) = \arccos(0.9118) = 24.24^{\circ} \tag{24}$$

$$P_{Id}\overrightarrow{LS}(CSA) = \frac{\left\|\overrightarrow{LS}(CSA)\right\|\cos\theta(\overrightarrow{LS}(CSA))}{\sqrt{\alpha^2 + \beta^2 + \gamma^2}} = \frac{0.2045\times 0.9118}{0.6124} = 0.3045 \tag{25}$$

Table 11. Vector-based results with respect to the three alternatives

Process	Composite Performance			Sustainability Magnitude	Sustainability Angle	Normalized Projection	Ranking
	En	*Ec*	*So*				
CSA	0.2689	0.5966	0.1549	0.2045	24.24°	0.3045	3
NHA	0.5275	0.6445	0.2277	0.3143	14.42°	0.4970	2

HHA	0.7799	0.1569	0.6174	0.4212	19.35°	0.6490	1
Ideal	1	1	1	0.6124	0°	1	-

According to Table 11, the longest sustainability magnitude (column 5) implies that the HHA route, which has significant advantages in the environmental benefits (column 2) and social responsibility (column 4), is the most sustainable process according to the absolute sustainability magnitude. However, the sustainability angle (column 6) indicates that the most balanced sustainability performance exists in the NHA pathway, while the second one is the HHA route for its economic performance (column 3) lags far behind compared with the other two pillars' performances. The normalized vector projection values (column 7) demonstrate that the HHA process has the best ultimately sustainability performance by incorporating both the absolute sustainability magnitude and the relative sustainability angle, providing a more comprehensive assessment result. Although being slightly ahead of the HHA in the sustainability angle, the ultimately sustainability of another promising process NHA ranks at the second place for its relatively weak performance in the magnitude compared to the HHA. The CSA process, the most traditional ammonia synthesis route, gets the lowest sustainability projection value from the life cycle perspective for its poor performance in the environmental and social pillars as well as the largest deviation from the totally sustainable direction.

Inspired by the idea of Moradi-Aliabadi and Huang[5] to quantify the deviation of the sustainability status of a system from the totally balanced development path, the methodology developed in this study integrates the magnitude and direction of the 3D sustainability vector into a projection value to characterize the ultimate sustainability performance of a system, which offers a more rigorous way for prioritizing alternatives' sustainability by eliminating the decision-making confusion that a process may act better in the magnitude but worse in the direction, or vice versa.

4. RESULTS COMPARISON

In this subsection, the proposed methodology and the prioritization results were analyzed by (1) comparison with the results obtained by using the existing methods; (2) sensitivity analysis for identifying the most critical pillar and criterion.

4.1 Comparison with the Existing Methods.

To verify the effectiveness of the proposed methodology, the sustainability ranking of the alternative ammonia production processes was also prioritized by employing two popular MCDM methodologies, i.e. the AHP-based Weighted Sum Model (WSM)[42] and the Technique for Order Preference by Similarity to an Ideal Solution (TOPSIS) method.[32] By using the same data with respect to each criterion and the relative weights regarding to the three pillars and categorized criteria, an identical priority sequence of the overall sustainability was obtained by using the two existing methods as that deprived from the proposed vector-based 3D LCSA methodology (Table 12), demonstrating the validity of the proposed assessment method. Comparing with the conventional MCDM methods that rely on "aggregated scores"[37] to rank the sequence, the 3D methodology could provide a more comprehensive and rigorous sustainability assessment by applying the vector analysis technique, which is characterized by not only considering the sustainability score, but also addressing the deviation of the sustainability performance of a process from the ideal direction.

Table 12. The sustainability sequence results by the existing methodologies

Methods	SWM-AHP		TOPSIS	
	Score	Rank	Score	Rank
CSA	0.3223	3	0.3117	3
NHA	0.4818	2	0.6118	2
HHA	0.5835	1	0.7053	1

4.2 Sensitivity Analysis.

In the developed methodology, the weights with respect to the three pillars and categorized criteria for the prioritization are obtained according to the experts' subjective descriptions, which vary with the experts' preferences and backgrounds. To investigate the robustness of the prioritization results, a novel sensitivity analysis method was proposed by extending the method introduced by Triantaphyllou and Sanchez[43] to identify the most critical pillar and criterion that will reverse the ranked sequence of the alternatives with the minimum change in its weight. To be specific, the identification of the most critical and sensitive pillar (or criterion) is conducted by altering the original weight of an investigated pillar (or criterion) while keeping the weights regarding to the other pillars and criteria invariant. Since weights of the pillars and criteria are determined in independent steps, the critical pillar and criteria were determined separately.

Criteria pillar identification. Assuming $P_i \succ P_j$ according to the proposed vector-based algorithm, but the decision-makers want to alter the current sequence by modifying the weight of one pillar. Taking the environmental pillar as an example, let $\delta_{\alpha,i-j}$ denotes the smallest change in the current weight α to reverse the prioritization ranking of alternatives P_i and P_j. In order to preserve the sum of the pillars' weights equals to 1, the weights regarding to the three pillars should be renormalized according to eq 26.

$$\alpha' = \frac{\alpha\text{-}\delta_{\alpha,i-j}}{\alpha\text{-}\delta_{\alpha,i-j} + \beta + \gamma} = \frac{\alpha\text{-}\delta_{\alpha,i-j}}{1-\delta_{\alpha,i-j}}$$
$$\beta' = \frac{\beta}{\alpha\text{-}\delta_{\alpha,i-j} + \beta + \gamma} = \frac{\beta}{1-\delta_{\alpha,i-j}} \quad (26)$$
$$\gamma' = \frac{\gamma}{\alpha\text{-}\delta_{\alpha,i-j} + \beta + \gamma} = \frac{\gamma}{1-\delta_{\alpha,i-j}}$$

Subsequently, based-on eq 15, to reverse the original ranking, $P_j\text{-}P_i \geq 0$ should be satisfied as shown in eq 27:

$$P_{ld}\overrightarrow{LS}(j) - P_{ld}\overrightarrow{LS}(i) = \frac{En(j)\times\alpha'^2 + Ec(j)\times\beta'^2 + So(j)\times\gamma'^2}{\alpha'^2+\beta'^2+\gamma'^2} - \frac{En(i)\times\alpha'^2 + Ec(i)\times\beta'^2 + So(i)\times\gamma'^2}{\alpha'^2+\beta'^2+\gamma'^2}$$
$$= \frac{(En(j)\text{-}En(i))\times(\frac{\alpha\text{-}\delta_{\alpha,i-j}}{1-\delta_{\alpha,i-j}})^2 + (Ec(j)\text{-}Ec(i))\times(\frac{\beta}{1-\delta_{\alpha,i-j}})^2 + (So(j)\text{-}So(i))\times(\frac{\gamma}{1-\delta_{\alpha,i-j}})^2}{(\frac{\alpha\text{-}\delta_{\alpha,i-j}}{1-\delta_{\alpha,i-j}})^2 + (\frac{\beta}{1-\delta_{\alpha,i-j}})^2 + (\frac{\gamma}{1-\delta_{\alpha,i-j}})^2} \geq 0 \quad (27)$$

Since $(\frac{\alpha\text{-}\delta_{\alpha,i-j}}{1-\delta_{\alpha,i-j}})^2 + (\frac{\beta}{1-\delta_{\alpha,i-j}})^2 + (\frac{\gamma}{1-\delta_{\alpha,i-j}})^2 > 0$, and $(\frac{1}{1-\delta_{\alpha,i-j}})^2 > 0$, eq 27 can be converted to eq 28:

$$(En(j)\text{-}En(i))\times(\alpha\text{-}\delta_{\alpha,i-j})^2 \geq (Ec(i)\text{-}Ec(j))\times\beta^2 + (So(i)\text{-}So(j))\times\gamma^2 \quad (28)$$

Here, the quantity of $\delta_{\alpha,i-j}$ can be calculated by eq 29:

$$\delta_{\alpha,i-j} \leq \alpha\text{-}\sqrt{\frac{(Ec(i)\text{-}Ec(j))\times\beta^2 + (So(i)\text{-}So(j))\times\gamma^2}{(En(j)\text{-}En(i))}}, \quad \text{if}\,(En(j)\text{-}En(i) > 0) \text{ or,}$$
$$\delta_{\alpha,i-j} \geq \alpha\text{-}\sqrt{\frac{(Ec(i)\text{-}Ec(j))\times\beta^2 + (So(i)\text{-}So(j))\times\gamma^2}{(En(j)\text{-}En(i))}}, \quad \text{if}\,(En(j)\text{-}En(i) < 0) \quad (29)$$

Obviously, the condition in eq 30 with respect to each pillar should be respectively satisfied for the value to be feasible.

$$
\begin{aligned}
&\text{For}En: \frac{(Ec(i)\text{-}Ec(j))\times\beta^2+(So(i)\text{-}So(j))\times\gamma^2}{(En(j)\text{-}En(i))}\geq 0\\
&\text{For}Ec: \frac{(En(i)\text{-}En(j))\times\alpha^2+(So(i)\text{-}So(j))\times\gamma^2}{(Ec(j)\text{-}Ec(i))}\geq 0\\
&\text{For}So: \frac{(En(i)\text{-}En(j))\times\alpha^2+(Ec(i)\text{-}Ec(j))\times\beta^2}{(So(j)\text{-}So(i))}\geq 0
\end{aligned} \tag{30}
$$

According to the above equations, one can see that the percentage of weight change with respect to each pillar should be respectively equal to Eq31.

$$
\begin{aligned}
&\text{For}En: \delta'_{\alpha,i-j}=\left[\alpha\text{-}\sqrt{\frac{(Ec(i)\text{-}Ec(j))\times\beta^2+(So(i)\text{-}So(j))\times\gamma^2}{(En(j)\text{-}En(i))}}\right]\times\frac{100}{\alpha}\\
&\text{For}Ec: \delta'_{\beta,i-j}=\left[\beta\text{-}\sqrt{\frac{(En(i)\text{-}En(j))\times\alpha^2+(So(i)\text{-}So(j))\times\gamma^2}{(Ec(j)\text{-}Ec(i))}}\right]\times\frac{100}{\beta}\\
&\text{For}So: \delta'_{\gamma,i-j}=\left[\gamma\text{-}\sqrt{\frac{(En(i)\text{-}En(j))\times\alpha^2+(Ec(i)\text{-}Ec(j))\times\beta^2}{(So(j)\text{-}So(i))}}\right]\times\frac{100}{\gamma}
\end{aligned} \tag{31}
$$

The critical criterion identification. Since only one criterion (En_1) exists in the economic pillar, making its weight (b_1=1) cannot be changed. Therefore, the three criteria in environmental pillar, and the three criteria in social pillar were investigated respectively. Taking the En_1 in the environmental pillar as an example, $\delta_{En_1,i-j}$ denotes the minimal change in the current weight a_1 for altering the sequence of $P_i \succ P_j$. Likewise, the weights regarding to three criteria in the environmental pillar should be renormalized according to eq 32.

$$
\begin{aligned}
&a_1'=\frac{a_1\text{-}\delta_{En_1,i-j}}{a_1\text{-}\delta_{En_1,i-j}+a_2+a_3}=\frac{a_1\text{-}\delta_{En_1,i-j}}{1-\delta_{En_1,i-j}}\\
&a_2'=\frac{a_2}{a_1\text{-}\delta_{En_1,i-j}+a_2+a_3}=\frac{a_2}{1-\delta_{En_1,i-j}}\\
&a_3'=\frac{a_3}{a_1\text{-}\delta_{En_1,i-j}+a_2+a_3}=\frac{a_3}{1-\delta_{En_1,i-j}}
\end{aligned} \tag{32}
$$

Subsequently, to reverse the ranking, $P_j\text{-}P_i \geq 0$ should be satisfied as shown in eq 33:

$$P_{Id}\overrightarrow{LS}(j)-P_{Id}\overrightarrow{LS}(i)=\frac{En(j)'\times\alpha^2+Ec(j)\times\beta^2+So(j)\times\gamma^2}{\alpha^2+\beta^2+\gamma^2}-\frac{En(i)'\times\alpha^2+Ec(i)\times\beta^2+So(i)\times\gamma^2}{\alpha^2+\beta^2+\gamma^2}$$
$$=\frac{(En(j)'\text{-}En(i)')\times\alpha^2+(Ec(j)\text{-}Ec(i))\times\beta^2+(So(j)\text{-}So(i))\times\gamma^2}{\alpha^2+\beta^2+\gamma^2}\geq 0 \quad (33)$$

Where $En(i)'=\frac{a_1\text{-}\delta_{En_1,i-j}}{1-\delta_{En_1,i-j}}\times En_1(i)+\frac{a_2}{1-\delta_{En_1,i-j}}\times En_2(i)+\frac{a_3}{1-\delta_{En_1,i-j}}\times En_3(i)=\frac{En(i)-\delta_{En_1,i-j}\times En_1(i)}{1-\delta_{En_1,i-j}}$,

and since $1-\delta_{En_1,i-j}>0$, Eq 33 can be converted to Eq 34:

$$\frac{\frac{(En(j)-En(i))\times\alpha^2-\delta_{En_1,i-j}\times(En_1(j)-En_1(i))\times\alpha^2}{1\text{-}\delta_{En_1,i-j}}+(Ec(j)\text{-}Ec(i))\times\beta^2+(So(j)\text{-}So(i))\times\gamma^2}{\alpha^2+\beta^2+\gamma^2}$$
$$=\frac{(En(j)-En(i))\times\alpha^2-\delta_{En_1,i-j}\times(En_1(j)-En_1(i))\times\alpha^2+(1-\delta_{En_1,i-j})\times\left[(Ec(j)\text{-}Ec(i))\times\beta^2+(So(j)\text{-}So(i))\times\gamma^2\right]}{\alpha^2+\beta^2+\gamma^2}$$
$$=P_{Id}\overrightarrow{LS}(j)-P_{Id}\overrightarrow{LS}(i)-\frac{\delta_{En_1,i-j}\times(En_1(j)-En_1(i))\times\alpha^2}{\alpha^2+\beta^2+\gamma^2}-\frac{\delta_{En_1,i-j}\times\left[(Ec(j)\text{-}Ec(i))\times\beta^2+(So(j)\text{-}So(i))\times\gamma^2\right]}{\alpha^2+\beta^2+\gamma^2} \quad (34)$$
$$=P_{Id}\overrightarrow{LS}(j)-P_{Id}\overrightarrow{LS}(i)-\delta_{En_1,i-j}\times(P_{Id}\overrightarrow{LS}(j)-P_{Id}\overrightarrow{LS}(i))+\delta_{En_1,i-j}\times\frac{\alpha^2}{\alpha^2+\beta^2+\gamma^2}\times(En(j)-En(i)-En_1(j)+En_1(i))\geq 0$$

Here, the quantity of $\delta_{En_1,i-j}$ can be calculated by Eq 35:

$$\delta_{En_1,i-j}\leq\frac{P_{Id}\overrightarrow{LS}(j)-P_{Id}\overrightarrow{LS}(i)}{(P_{Id}\overrightarrow{LS}(j)-P_{Id}\overrightarrow{LS}(i))-(En(j)-En(i)-En_1(j)+En_1(i))\times\frac{\alpha^2}{\alpha^2+\beta^2+\gamma^2}}$$
$$\text{if}\,(P_{Id}\overrightarrow{LS}(j)-P_{Id}\overrightarrow{LS}(i))-(En(j)-En(i)-En_1(j)+En_1(i))\times\frac{\alpha^2}{\alpha^2+\beta^2+\gamma^2}>0 \text{ or,}$$
$$\delta_{En_1,i-j}\geq\frac{P_{Id}\overrightarrow{LS}(j)-P_{Id}\overrightarrow{LS}(i)}{(P_{Id}\overrightarrow{LS}(j)-P_{Id}\overrightarrow{LS}(i))-(En(j)-En(i)-En_1(j)+En_1(i))\times\frac{\alpha^2}{\alpha^2+\beta^2+\gamma^2}} \quad (35)$$
$$\text{if}\,(P_{Id}\overrightarrow{LS}(j)-P_{Id}\overrightarrow{LS}(i))-(En(j)-En(i)-En_1(j)+En_1(i))\times\frac{\alpha^2}{\alpha^2+\beta^2+\gamma^2}<0$$

Obviously, the following condition in Eq 36 with respect to each criterion in the environmental or social pillar should be respectively satisfied for the value to be feasible:

$$\text{For}\,En_k: a_k-\delta_{En_k,i-j}\geq 0$$
$$\text{For}\,So_k: \gamma_k-\delta_{So_k,i-j}\geq 0 \quad (36)$$

According to the above formulas, the percentage of weight change with respect to each criterion in the environmental and social pillar can be respectively determined as

Eq 37.

$$\text{For}En_k : \delta'_{En_k,i-j} \le \frac{P_{Id}\overrightarrow{LS}(j) - P_{Id}\overrightarrow{LS}(i)}{(P_{Id}\overrightarrow{LS}(j) - P_{Id}\overrightarrow{LS}(i)) - (En(j) - En(i) - En_k(j) + En_k(i)) \times \frac{\alpha^2}{\alpha^2+\beta^2+\gamma^2}} \times \frac{100}{\alpha_k}$$

$$\text{For}So_k : \delta'_{So_k,i-j} \le \frac{P_{Id}\overrightarrow{LS}(j) - P_{Id}\overrightarrow{LS}(i)}{(P_{Id}\overrightarrow{LS}(j) - P_{Id}\overrightarrow{LS}(i)) - (So(j) - So(i) - So_k(j) + So_k(i)) \times \frac{\gamma^2}{\alpha^2+\beta^2+\gamma^2}} \times \frac{100}{c_k} \quad (37)$$

Based on the reference,[43] the following definitions were introduced to investigate the criticality and sensitivity of the assessment element (pillar or criterion):

Definition 1. The percentage-top (*PT*) critical element demonstrates that P_j can replace P_i as the best alternative with the minimum percentage of weight change $\left|\delta'_{element,i\text{-}j}\right|$.

Definition 2. The percentage-any (*PA*) critical element refers to the element that reverse the rank of any alternatives P_i and P_j with the minimum percentage of weight change $\left|\delta'_{element,i\text{-}j}\right|$.

Definition 3. The criticality degree (*CD*) is the smallest $\left|\delta'_{element,i\text{-}j}\right|$ value regarding to the investigated element.

Definition 4. The sensitivity coefficient (*SC*) of is the reciprocal value $\frac{1}{\left|\delta'_{element,i\text{-}j}\right|}$ of the CD regarding to the investigated element.

By conducting the proposed sensitivity analysis, the minimum percentage of weight change to reverse the alternative pairs, as well as the criticality degree and the sensitivity coefficient information with respect to each pillar and criterion were illustrated in Tables 13 and 14. As for the pillars, although the environmental pillar was recognized as both the *PT* critical (Definition 1) and the *PA* critical pillar (Definition 2) with the smallest weight change of 68.87%, the weight of the economic pillar should also be addressed accurately for its *CD* (Definition 3) and *SC* (Definition 4) values are pretty close to those of the environmental pillar. The social pillar was deemed to be non-critical and insensitive, demonstrating that the sustainability sequence stands invariant no matter how the weight of the social pillar fluctuates while the others remain unchanged. As for the environmental and social criteria, the global warming (En_1) was identified as both the *PT* and *PA* critical criterion, implying that the accurate determination of the weight of En_1 is crucial for ranking the alternatives correctly and accurately. The priority rank of the alternative processes could also experience an alternation with a dramatic decrease in the weight of abiotic depletion (En_2), or even a larger change in the weight of energy efficiency (En_3). However, all the three criteria in the social pillar belong to the non-critical and insensitive type, indicating that the weight change in a social criterion has no significant effect on the final ranking. Moreover, since only the criterion of life cycle costs (Ec_1) is considered in the economic pillar, the analysis result for the economic pillar could represent the criticality and sensitivity for the Ec_1 criterion, demonstrating that a careful weight determination on Ec_1 is necessary.

Table 13. Sensitivity analysis result of the pillars

Pair	*En*	*Ec*	*So*
HHA-CSA	N/F	-138.76	N/F
HHA-NHA	68.87	-69.41	N/F
NHA-CSA	N/F	N/F	N/F
CD	68.87	69.41	Non-critical
SC	0.0145	0.0144	Insensitive

N/F (non-feasible) due to the dissatisfaction of Eq 30.

Table 14. Sensitivity analysis result of the criteria

Pair	En_1	En_2	En_3	So_1	So_2	So_3
HHA-CSA	98.87	-9617.43	-100662.7	N/F	N/F	N/F
HHA-NHA	N/F	N/F	N/F	N/F	N/F	N/F
NHA-CSA	N/F	-242.34	-1022.95	N/F	N/F	N/F
CD	98.87	242.34	1022.95	Non-critical	Non-critical	Non-critical
SC	0.0101	0.0041	0.0010	Insensitive	Insensitive	Insensitive

Notes: N/F (non-feasible) due to the dissatisfaction of Eq 36.

It is worthy pointing out that the sustainability priority of the case study is based on the current status of these process alternatives, which could change with the process development as well as the variation of decision-makers' preferences. Therefore, a comprehensive, adequate and representative criteria system is a prerequisite for the sustainability assessment, while more precise data with respect to the hard criteria as well as more thorough investigation of the experts' preferences regarding the soft criteria and the weights determination can make the assessment result more reliable.

5. DISCUSSION AND CONCLUSIONS

This paper outlines an integrated vector-based 3D mathematical framework for the life cycle sustainability assessment and prioritization of alternative chemical processes. In the methodology, a 3D sustainability criteria system in a life cycle perspective is established by using the LCA, LCC, and S-LCA methods, respectively, which is able to simultaneously consider the environmental performance, economic impact, and social issues of the alternatives. The methodology incorporates the AHP method to quantify the soft criteria, therefore, it is able to achieve a comprehensive sustainability assessment by considering both the hard criteria using quantitative assessment and soft criteria based on the knowledge-based qualitative evaluation. Finally, a 3D vector is formulated to characterize the sustainability performance of a chemical process, with the magnitude indicating the absolute sustainability performance, the angle quantifying the deviation of the sustainability performance from the totally sustainable direction, the normalized vector projection comparing the overall sustainability of the alternatives by incorporating both the magnitude and direction of the investigated vector. The developed methodology was illustrated by a case study of the sustainability assessment and prioritization of three ammonia production processes. The effectiveness of the developed methodology was analyzed by comparing with the existing MCDM methodologies, while the robustness of the assessment result was analyzed by identifying the most critical pillar and criterion.

The proposed methodology provided a mathematical framework for the life cycle sustainability assessment of alternative chemical processes, however, a couple of limitations existing in the current study need to be improved in the future studies: (1) the data for the hard criteria in the case study were collected from the scattered literature resources, which might be inconsistent and imperfect, while the soft criteria were scored according to the experts' judgments, which inevitably involve subjectivities and vagueness, therefore, the uncertainties associated with the input data and information should be considered in the future; (2) the criteria/pillars presented in this study were assumed to be independent, which could yield an unreliable result if interactive or influential relationships exist among the criteria and pillars, accordingly, the interactions between the assessment pillars and criteria should be further addressed in the future study.

Supporting Information

The random index (Table S1)

This information is available free of charge via the Internet at http://pubs.acs.org/.

The Supporting Information is available free of charge on theACS Publications website at DOI: 10.1021/acs.iecr.7b02041.

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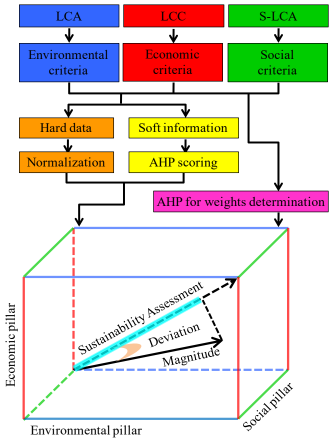

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