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A Green Chemistry-based Decision Modelling Approach for Optimal Selection of Nanomaterial's Synthesis Method

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Recent advances in nanotechnology have produced materials with superior performance in various industrial applications including medicine and advanced manufacturing. Synthesis of these so-called nanomaterials within the guiding philosophy of green chemistry has also continuously gaining attentions among researchers to address such emerging issue of sustainability. Green chemistry provides a set of principles which encourages the alternative design of product and processes that use renewable feedstock, and are energy efficient and safer with less hazardous pathway toward synthesis. However, optimal selection of such green synthesis method is a complex decision making problem that requires an integration of both tangible and intangible criteria. This work thus develops a metric from a green chemistry-inspired hierarchical decision model in prioritizing different synthesis methods of nanomaterial. A Monte Carlo simulation-aided Fuzzy Analytic Hierarchy Process (FAHP) coupled with Grey Relational Analysis (GRA) was used to rank the alternatives by integrating the knowledge from both peer-reviewed literature and experts in the field, while addressing the uncertainty involved in the decision making process. Such approach makes also the decision making transparent and open for new perspectives or criteria whenever relevant data becomes available. An illustrative example is presented for a case study of carbon nanotube synthesis.

1. Introduction

The past decade has seen the immense rise of nanotechnology as reflected in the significant increase in the number of scientific papers published and patents granted (Chen et al, 2013). The impact of nanotechnology in discovery and innovation can be attributed to the novel properties nanomaterials demonstrate, which are not exhibited by their bulk counterparts. For instance, bulk gold is inert while nano-sized gold particles are catalytically active (Bond & Thompson, 1999). In addition, carbon nanotubes exhibit unusual electronic, thermal, and mechanical properties which are not observed for the typical bulk carbon (Dresselhaus et al., 2004). As a consequence, nanomaterials have found widespread applications in medicine (Salata, 2004), agriculture (Khot et al, 2012), defense (Reynolds & Hart, 2004), among others. Considering that these novel and useful properties are size-dependent, the method of nanomaterial synthesis represents an active area of research in nanotechnology. Synthetic methodologies that provide high degrees of control over the morphology and properties of the nanomaterials are thus highly sought after. With the advent and development of numerous synthetic processes for tailor-made nanomaterials, concerns regarding the safety and efficiency of each method have emerged (Hutchinson, 2008). This has led to the synthesis of nanomaterials within the guiding philosophy of green chemistry in order to address the issues of sustainability and safety. Green chemistry provides a set of principles that encourages the alternative design of product and processes that use renewable feedstock, and are energy efficient and safer with less hazardous pathway toward synthesis (Mulvihill et al, 2011). Models have been thus created in order to aid the decision-making process on which synthetic process best suits a particular concern. The tools which have been used to create these models include multi-criteria decision analysis such as outranking method (Linkov et al, 2011), life cycle assessment (Hischier & Walser, 2012), a combination of both (Seager and Linkov, 2008), among others. However, optimal selection of such green synthesis method is a complex decision making problem under

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uncertainty that requires an integration of both tangible and intangible criteria in the evaluation process. This work thus introduces a metric based from a green chemistry-inspired hierarchical decision model in prioritizing different synthesis methods of nanomaterial. A hybrid multiple criteria decision model was developed that integrates Fuzzy Analytic Hierarchy Process (FAHP) and Grey Relational Analysis (GRA) to measure the so-called green synthesis potential of the different alternative synthesis methods. FAHP provides the systematic procedure to make explicit the preference of the decision maker while addressing the vagueness of judgments in deriving the weights of the criteria. On the other hand, GRA provides a simple but intuitive method to measure the relative desirability of an alternative based on its closeness to an idealized alternative. In this study, a Monte Carlo simulation-aided computation of the green synthesis potential-cost ratio was used to rank the alternatives by integrating the knowledge from both peer-reviewed literature and domain experts in the field, while addressing the uncertainty involved in the evaluation process. A case study on carbon nanotube synthesis is thus presented to demonstrate the proposed technique.

2. Methodology

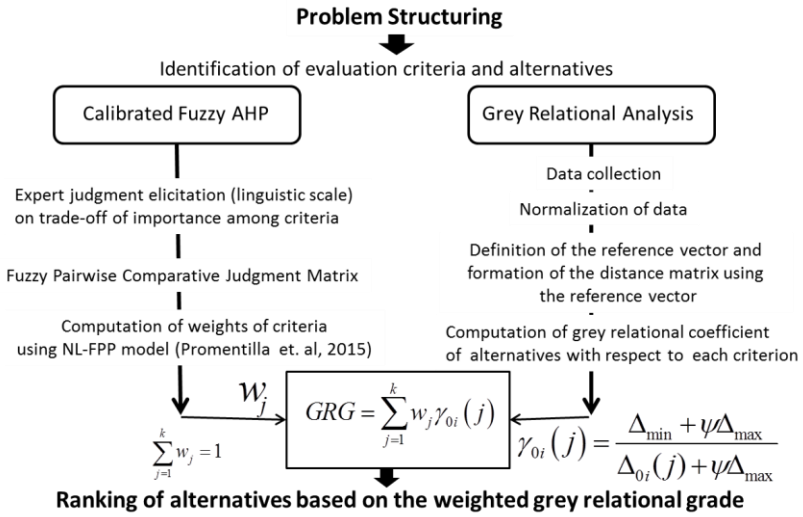


Figure 1: A decision modelling approach based on Fuzzy AHP and GRA (Eusebio et. al.,2016).

The proposed decision modelling approach for the optimal selection of nanomaterial's synthesis method is based on the integrated FAHP-GRA as described in Figure 1. The problem structuring phase involves the identification of evaluation criteria inspired from the green chemistry principles. The structure is then described in a hierarchical manner such that the goal, i.e., measuring the green synthesis potential, is the uppermost level in the structure followed by the set of multi-level criteria. The alternatives that will be evaluated are then identified and placed at the lowermost level in the structure. In the second phase, the relative importance of the criteria is measured through the Fuzzy Analytic Hierarchy Approach (FAHP). This technique is a variant of AHP, which is one of the widely used pairwise comparison techniques to derive weights from verbal judgments (Saaty, 1977). But instead of using Saaty's fundamental 9-point scale, the verbal judgments are described as triangular fuzzy numbers (TFN) to address the ambiguity of the judgments elicited from the stakeholders or experts. The proposed fuzzy scale which follows the Fibonacci sequence as shown in Table 1 is based on a recent study of Promentilla et.al. (2016).

For example, when a *criterion i* is perceived as moderately more important than *criterion j*, the verbal judgment (a_{ij}) can be approximated by a TFN <l_{ij}, m_{ij}, u_{ij}>. The triples <1.2, 2, 3.2> represent the lower bound, modal value, and upper bound of the TFN for the vague term "moderately more". Note that the degree of fuzziness, i.e., the difference between the upper bound and lower bound, is described to be greater to those verbal judgments of "strongly more" and "very strongly more". The calibration of such membership function of these fuzzy numbers is based from real pairwise comparisons of measurable properties such as that of area of geometrical figures (Ishizaka and Nguyen, 2013).

Table1: Calibrated Fuzzy Scale

Linguistic scale	Fuzzy number	Lower bound	Modal value	Upper bound
Equally	1	1.0	1	1.0
Moderately	2	1.2	2	3.2
Strongly	3	1.5	3	5.6
Very strongly	5	3.0	5	7.9
Absolutely	8	6.0	8	9.5

For multiple experts or decision makers, these individual judgments of *K* respondents are then aggregated using the geometric mean method (Promentilla et al, 2015). After the pairwise comparison, the matrix is filled up with these fuzzy numbers, and a nonlinear fuzzy preference programming approach described in Promentilla et al. (2015) is used to approximate the ratio-scale weights (w_j) of *n* criteria that will maximize the λ. This nonnegative λ can be used as a measure of consistency wherein the ratio of these computed weights also satisfy the initial fuzzy judgments obtained from at least (*n-1*) pairwise comparative judgments. A λ of 1.0 indicates perfect consistency whereas a λ of 0.0 indicates fuzzy judgments are only satisfied at their boundaries (Tan et al., 2014). Note that the global weights of the criteria from FAHP are then used for the computation of the weighted grey relational grade (GRG) in the third phase (Eusebio et al., 2016).

In general, the concept of GRG is derived from the grey relational analysis (GRA) proposed by Deng (1989) as a measure of the magnitude of correlation between reference series and comparison series. For the purpose of brevity, the details of this procedure for multi-criteria decision analysis is not discussed in this paper but can be found elsewhere (e.g., see Kuo et al. (2008)). The GRG is essentially a generalized distance function such that the closer the alternative to the reference or idealized alternative, the higher the value of GRG is. As the collected data such as performance scores or rating may have different units, these must be normalized to a dataset with values ranging between 0 and 1 inclusive wherein 1 denotes the idealized score (best performance). In this study, a simplified 5-point Likert scale was used to evaluate the potential of an alternative to satisfy the green synthesis criteria. A rating of "1" means very low potential whereas a rating of 5 means very high potential with respect to the criterion. The resulting normalized matrix (with size of *n x k*) is composed of comparison series ($x^*_i(j)$), i.e., row vectors of *n* compared alternatives containing normalized data of *k* performance scores. Note that the reference series ($x_o(j)$) is denoted by row vector of *1*s. This reference series is used to generate the distance matrix which is the difference or distance ($\Delta_{0i}(j)$) between the reference value and each comparison value. In this distance matrix, the minimum difference (Δmin) and maximum difference (Δmax) was used to compute the grey relational coefficient as shown in Eq.(1):

$$\gamma_{0i}(j) = \frac{\Delta_{\min} + \psi\Delta_{\max}}{\Delta_{0i}(j) + \psi\Delta_{\max}} \tag{1}$$

The distinguishing coefficient (ψ) with a typical value of 0.50 is just used to expand or compress the range of grey relational coefficient. The GRG of each alternative is then computed as the weighted sum of the grey relational coefficients for all the criteria as described in Eq.(2):

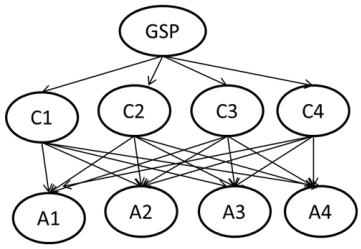
$$GRG = \sum_{j=1}^{k} w_j \gamma_{0i}(j) \tag{2}$$

Such GRG score can be interpreted as a metric for green synthesis potential (GSP) of an alternative wherein a GRG score of 1.0 is the idealized alternative for green synthesis. The closer the GRG score to 1.0, the more desirable the alternative is for green synthesis. This green synthesis potential metric divided by the normalized cost is a green synthesis index (GSI) that can be used to rank the alternatives. This ratio has an idealized value of 1, and is analogous to the benefit-cost ratio wherein the higher the value is, the better the alternative is. Note that the cost of the alternatives is normalized with the minimum value such that the least cost alternative is the reference alternative and will have a normalized cost of 1.0.

In the fourth phase, Monte Carlo (MC) simulation is then used for uncertainty analysis of the computed GSI to account for the variability in the ratings provided by the experts to measure the green synthesis potential and also for the uncertainty associated with the cost estimation of the alternative. The variability in these model parameters is simulated by assuming a specific probability distribution. As for this study, the desirability rating is modeled as a uniform distribution and the cost is modeled as a triangular distribution.

3. An illustrative case study: selection of carbon nanotube synthesis methods

In this case study, it is assumed that in the product development stage of selecting the most promising technology for synthesizing carbon nanotubes will involve criteria that are consistent with the green chemistry principles. No single criterion such as the highest material efficiency or least cost will be considered as the only decisive factor to choose the best alternative. Four criteria were identified as follows: 1) potential for pollution reduction, lower life-cycle environmental impact including the degradation of the product (C1); 2) potential for higher material efficiency and use of renewable feedstock (C2); 3) potential for higher energy efficiency (C3); and 4) potential for lower risk in terms of hazard and toxicity (C4). As illustrated in Figure 2, alternatives are evaluated based from these 4 criteria. There are feasible process technologies to synthesize carbon nanotubes namely, High Pressure Carbon Monoxide (A1), arc discharge (A2), chemical vapor deposition (A3), and laser vaporization (A4). Chemical vapour deposition involves the vaporization of a carbon source in a high-vacuum environment. The vaporized carbon source will then be deposited on the surface of a metal catalyst where nanotube growth will occur (Cassel et al., 1999). Similarly, HiPCO is a large-scale carbon nanotubes production technique that involves flowing carbon monoxide on catalytic clusters in a high pressure and high temperature environment (Nikolaev et al, 1999). The arc discharge and laser ablation methods share a similar principle of carbon nanotubes synthesis. Either an arc discharge or laser is used to vaporize graphite pellets to initiate the nanotube formation (Prasek et al, 2011).



Nomenclature	
GSP: Green Synthesis Potential	
Criteria	Alternative
C1:Potential for pollution reduction, lower life-cycle environmental impact including the degradation of the product	A1: High Pressure Carbon Monoxide (HiPCO)
C2:Potential for higher material efficiency and use of renewable feedstock	A2: Arc Discharge (Arc)
C3:Potential for higher energy efficiency	A3: Chemical vapour deposition (CVD)
C4: Potential for lower risk in terms of hazard and toxicity	A4: Laser vaporization (Laser)

Figure 2: The decision hierarchy for the optimal selection of carbon nanotube synthesis.

Table 2: Pairwise comparative judgement matrix from group fuzzy judgments and the computed weights

	C1	C2	C3	C4	Weights (λ=0.56)
C1	<1,1,1>	<0.33,0.38,0.69>	<0.65,0.65,1.36>	<0.38,0.43,1.10>	0.14
C2		<1,1,1>	<0.83,0.99,2.86>	<0.75,0.85,2.16>	0.30
C3			<1,1,1>	<0.49,0.49,1.12>	0.22
C4				<1,1,1>	0.33

Table 3: Rating scores (min, max) of the alternatives with respect to each criterion

	C1	C2	C3	C4
A1 (HiPCO)	(3,5)	(2,4)	(2,4)	(2,4)
A2 (Arc)	(3,4)	(3,4)	(1,3)	(2,4)
A3 (CVD)	(2,3)	(3,4)	(2,3)	(2,4)
A3 (Laser)	(2,4)	(3,5)	(1,3)	(2,4)

Fuzzy AHP was used to quantify the relative importance of each criterion in measuring the green synthesis potential. Pairwise comparative judgment matrix was populated with the aggregated individual judgements from domain experts as shown in Table 2. Using the NLP model, priority vector was calculated with a fuzzy consistency index of 0.56. This result shows that the most important criterion is the potential for lower risk in terms of hazard and toxicity (C4) and the least important is potential for pollution reduction, lower life-cycle environmental impact including the degradation of the product (C1). GRA was then utilized in evaluating the desirability of each alternative based from the four criteria. The resulting GRA data are shown in Table 3, where the first and second numbers inside the parentheses represent the minimum and maximum ratings

respectively of alternative provided by the domain experts with respect to a criterion. The 5-point scale refers to very low (1), low (2), moderate (3), high (4), very high (5) potential to satisfy the criterion. Indication also suggests that the toxicity and health risks associated with each alternative are highly uncertain and the alternatives are evaluated with equal probabilities ranging from low to high potential to reduce such risk.
The sample decision matrix was summarized in Table 3 with the calculated green synthesis potential (GSP) based from GRG of each alternative at distinguishing coefficient (Ψ) of 0.50. The normalized cost for each alternative is based on the data provided by Linkov et al., (2011). GSI is then computed from the ratio of GSP to normalized cost which can be used to rank the alternatives. The closer the value to 1.0, the better the alternative is, i.e., consistent with the green chemistry framework. Indication suggests from this point-value estimate of GSI that the ranking is as follows: HiPCO > Laser > Arc > CVD. To treat the uncertainty involved in the evaluation process, MC simulations were done wherein the random variables are the rating with respect to each criterion and the cost of the alternatives. The rating follows a uniform distribution parameterized by the maximum and minimum value described in Table 3. On the other hand, a triangular distribution was used to model the uncertainty in cost based on a literature value (Linkov et al., 2011). Figure 3 describes the results of simulated GSI based on 10,000 simulations.

Table 3: Sample decision matrix for alternatives and computation of green synthesis index (GSI)

Alternatives	C1 (0.14)*	C2 (0.30)*	C3 (0.22)*	C4 (0.33)*	GSP	Norm-Cost	GSI (Rank)
A1 (HiPCO)	4	3	4	3	0.778	1.00	0.78 (1)
A2 (Arc)	4	3	2	3	0.667	3.52	0.19 (3)
A3 (CVD)	2	3	2	3	0.556	3.93	0.14 (4)
A3 (Laser)	3	4	3	3	0.704	1.65	0.43 (2)

**weights obtained from FAHP*

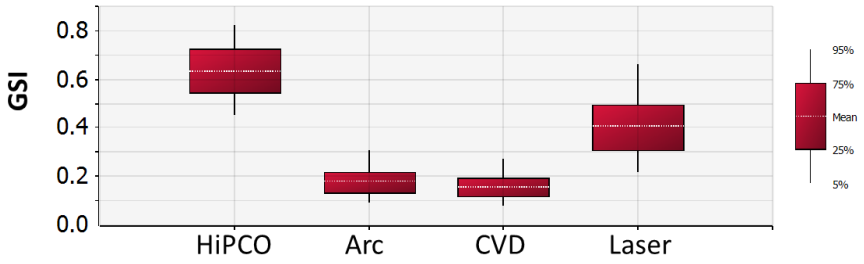


Figure 3: Box-whisker plot of simulated results of GSI for each alternative

Based on the median values of simulated GSI, A1 (HiPCO) is the most desirable alternative for carbon nanotube synthesis followed by A4 (Laser). However, both alternatives (A1 and A4) are the most sensitive to change compared to the other alternatives as indicated by length of their whisker. A3 (CVD) is the least desirable but the median GSI of A3 and A4 are close to each other. These two alternatives are also the least sensitive to changes in the rating and cost.

4. Conclusions

This work demonstrates the application of a decision modelling approach to the optimal selection of nanomaterial's synthesis method in particular to carbon nanotubes. Four alternatives (HiPCO, Arc, CVD, Laser) were evaluated according to green chemistry criteria. These criteria are the potential for pollution reduction, lower life-cycle environmental impact including the degradation of the product (C1); potential for higher material efficiency and use of renewable feedstock (C2), 3) potential for higher energy efficiency (C3), and potential for lower risk in terms of hazard and toxicity (C4). The green synthesis index is computed from the Monte Carlo aided Fuzzy AHP-GRA while addressing the uncertainty involved in the evaluation process. For this case study, the most desirable alternative for carbon nanotube synthesis is the high pressure carbon monoxide (HiPCO) technique followed by laser ablation. The proposed technique provides a simple but robust mathematical approach where results can be easily interpreted by decision makers. Such approach makes also the decision making process transparent and open for new perspectives or criteria whenever relevant

data becomes available. Literature on well-studied nanomaterials and expert judgments can be used for evaluation, as well as, for emerging technology in nanomaterials synthesis. Future work will also consider the sensitivity of model results on the weighting of the criteria and the restructuring of the decision hierarchy.

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