CHEMICAL ENGINEERING TRANSACTIONS
VOL. 94, 2022

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Yee Van Fan, Jiří J. Klemeš, Sandro Nižetić

ISBN 978-88-95608-93-8; **ISSN** 2283-9216

DOI: 10.3303/CET2294129

Optimal Selection of Materials for Hydrogen Solid-State Storage

Gian Paolo O. Bernardo*, Michael Angelo B. Promentilla

De La Salle University, 2401 Taft Ave., Malate, Manila, 1004, Philippines
gian.bernardo@dlsu.edu.ph

Hydrogen has been attracting interest as a clean and potentially sustainable energy vector for a multisectoral transition toward low-carbon emissions-based systems and economies. Recent trends in developing a hydrogen economy highlight the importance of hydrogen solid-state storage, along with production, distribution, and utilization. For purposes of storage, ongoing research efforts have considered several nanoporous materials such as carbonaceous materials, metal-organic frameworks, covalent organic frameworks, zeolites, inter-metallic hydrides, and others as promising materials. In this study, metal organic frameworks, carbonaceous materials, metal hydrides, and complex hydrides were evaluated using the fuzzy multi-criteria decision-making (FMCDM) technique to identify the optimal material in terms of surface area, capacity, dehydrogenation temperature, and stability for hydrogen storage. The method combined both quantitative and qualitative criteria in the decision structure wherein linguistic assessment under uncertainty is integrated into the decision model. A novel approach is proposed utilizing a normal distribution for the degree of indeterminacy in the linguistic scale. An illustrative case study is presented to rank the said materials for hydrogen solid-state storage. Results indicate that metal organic frameworks are the best alternative attributed to their relatively high surface area and excellent dehydrogenation temperature, while metal hydrides are the worst attributed to their relatively low surface area and sorption capacity. Sensitivity analysis was performed wherein a new approach to quantify ranking invariance and robustness is also introduced. Higher robustness values can be acquired by screening specific materials with tighter assessment virtues for selection or by narrowing down the domain of weights.

1. Introduction

The depletion of fossil fuels as a source of energy has resulted in increasing interest in alternative carriers of energy, such as hydrogen (Nicoletti, 1995). The viability of hydrogen as an energy carrier, with zero-emissions and production capacity from natural sources, has been well-established (Barthélémy, 2012). What remains a challenge is the storage of hydrogen for the efficient and convenient use of the energy it carries (Free et al., 2021). Specifically, due to the inherent costs and issues related to storing hydrogen in gaseous form (Züttel, 2004) and in liquid form through mechanical means such cryogenics (Ahluwalia et al., 2016), research work has been more focused on chemical storage processes such as solid-state methods (Zacharia and Rather, 2015).

The methods for the storage of solid-state hydrogen can be classified into four: metal-organic frameworks (MOFs), carbonaceous materials (CMs), metal hydrides (MHs), and complex hydrides (CHs) (Boateng and Chen, 2020). As each comes with their advantages and disadvantages (Andersson and Grönkvist, 2019), usually in terms of physical characteristics (surface area, sorption capacity), chemical characteristics (kinetics, stability), and costs, however, each of these classes would have a range of values instead of a specific numerical figure, e.g. 7 wt.% to 18 wt.% instead of 13 wt. %. In addition, the assignment-of-benefit is not an entirely objective process.

The selection of the “best” alternative is not always a straightforward process. In cases where alternatives can be classified and ranked based on certain criteria, such as in the case of hydrogen storage materials which can be assessed based on several physical and chemical characteristics, multi-criterion decision analysis (MCDA) aids in providing a structure in the decision-making process (Bystrzanowska and Tobiszewski, 2018). Furthermore, in cases where alternatives are not always ranked quantitatively, the use of fuzzy spherical sets

Paper Received: 15 May 2022; Revised: 29 June 2022; Accepted: 29 June 2022
Please cite this article as: Bernardo G.P., Promentilla M.A.B., 2022, Optimal Selection of Materials for Hydrogen Solid-State Storage, Chemical Engineering Transactions, 94, 775-780 DOI:10.3303/CET2294129

enables the determination of a more accurate and reliable assessment by taking into account the vagueness of the qualitative comparison.

In this study, a fuzzy multi-criteria decision-making (FMCDM) approach is taken with spherical fuzzy sets with linguistic performance scaling for defuzzification is demonstrated in identifying a class of materials suitable for solid-state hydrogen storage, with a novel calibrated normal distribution for indeterminacy.

2. Model formulation

Spherical fuzzy set is one of the most recent extensions of Zadeh's fuzzy set to address the ambiguity, imprecision and indeterminacy of human opinion as expressed in linguistic assessments that will be analogous to human thinking style of the decision-making process (Kuok and Promentilla, 2021). In this work, only the terms and variables necessary for the framework of the analysis are included. The readers are encouraged to seek more information about the development of spherical fuzzy methodology and the technique for order of preference by similarity to ideal solution (TOPSIS) elsewhere (Farrokhizadeh et al., 2021).

Defining μ, η, π as the degrees of membership, non-membership, and indeterminacy, respectively, where

$$\mu, \eta, \pi \rightarrow [0, 1] \tag{1}$$

and

$$0 \leq \mu^2 + \eta^2 + \pi^2 \leq 1 \tag{2}$$

the spherical fuzzy number S_n is designated as an ordered triple of the three-dimensional form (μ, η, π).

The scoring function, S_f, for the defuzzification of the fuzzy number is defined as

$$S_f = 1 - \left[\frac{(1-\mu^2)^\beta + (\eta^2)^\beta + (\pi^2)^\beta}{3}\right]^{\frac{1}{\beta}} \tag{3}$$

where $\beta \geq 1$ is the distance parameter.

Using an 11-level linguistic performance scale, the values of the distance parameter and for the normal distribution for indeterminacy were chosen such that the values of membership are all exactly ½ for the neutral assessment. With $\beta = 19/8$, Gaussian parameters $\bar{\pi} = 5$ and $\sigma_\pi = \sqrt{2}$, determined through Excel Solver with integer constraints, and with arithmetic scaling for indeterminacy, the linguistic performance scale was defuzzified as follows:

Table 1: Defuzzified linguistic performance scale

Linguistic Assessment	10-point scale	Symbol	μ	η	π	S_f
Ideal Best	10	IB	1.000	0.000	0.000	1.000
Excellent	9	EX	0.900	0.100	0.009	0.880
Very Good	8	VG	0.800	0.200	0.053	0.773
Good	7	GD	0.700	0.300	0.184	0.676
Above Satisfactory	6	AS	0.600	0.400	0.389	0.585
Satisfactory/Neutral	5	S	0.500	0.500	0.500	0.500
Below Satisfactory	4	BS	0.400	0.600	0.389	0.439
Bad	3	BD	0.300	0.700	0.184	0.375
Very Bad	2	VB	0.200	0.800	0.053	0.307
Worse	1	WO	0.100	0.900	0.009	0.236
Worst	0	W	0.000	1.000	0.000	0.157

Note that the distribution of indeterminacy follows a normal distribution, a novel proposal in this study. The numerical rating from the scoring function in Table 1 was used to defuzzify the evaluation matrix through TOPSIS calculations, defining x_{ij} as an element in evaluation matrix M with n number of alternatives, i, and m number of criteria, j, through the normalization of each of the matrix elements using

$$\bar{x}_{ij} = \frac{x_{ij}}{\sqrt{\sum_{i=1}^{n} {x_{ij}}^2}} \tag{4}$$

and then arithmetically weighted equally into w_{ij}. The defuzzified performance score of alternative i, thus, follows:

$$P_i = \frac{E_i^-}{E_i^+ + E_i^-} \tag{5}$$

where E_i^+ and E_i^- are the Euclidean distances of alternative i from the weighted best w_j^+ and the weighted worst w_j^- respectively as follows:

$$E_i^+ = \sqrt{\sum_{j=1}^{m} \left(w_{ij} - w_j^+\right)^2} \tag{6}$$

$$E_i^- = \sqrt{\sum_{j=1}^{m} \left(w_{ij} - w_j^-\right)^2} \tag{7}$$

The alternatives were then ranked based on the performance scores.

3. Optimal selection for solid-state hydrogen storage

Four alternative materials for hydrogen storage (MOFs, CMs, MHs, CHs) were evaluated using four criteria (surface area (SA), sorption capacity (SC), dehydrogenation temperature (DT), stability (ST)). The hierarchy of the FMCDM Problem is shown in Figure 1.

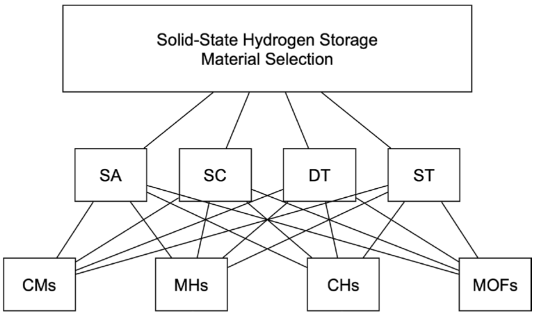


Figure 1: FMCDM Problem Structure and Hierarchy

From literature, the qualitative linguistic assessment of the alternative-criterion matrix was generated and shown in Table 2. Specifically, for example, the sorption capacities by weight were found to be 7.08 % for carbonaceous materials (Wang et al., 2009), 2.5 % to 6.5 % for metal hydrides (von Colbe et al., 2019), 14.90 % for complex hydrides (Ley et al., 2014), and 12.60 % for metal organic frameworks (Gómez-Gualdrón et al., 2017). However, not all have reported specific numerical values where a range is instead known, such as for the surface area where carbonaceous materials have 400 - 2,000 m^2/g (Benabithe, 2018), metal hydrides have 50 - 125 m^2/g (Fan et al., 2006), metal organic frameworks have 1,000 - 10,000 m^2/g (Furukawa et al., 2013), while complex hydrides have been said to have “high” surface area (Milanese et al., 2019). The same process was done for dehydrogentation temperature (DT) and stability (ST).

Table 2: Alternative-criterion matrix

	SA	SC	DT	ST
CMs	VG	AS	VG	AS
MHs	BS	BS	VG	EX
CHs	VG	EX	S	GD
MOFs	EX	VG	EX	VG

From the output of the scoring function in Table 1, the qualitative assessments in Table 2 were translated into numerical values, normalized using Eq(3), and subsequently weighted equally. The resulting values are shown in Table 3.

Table 3: Equally weighted assessments

	SA	SC	DT	ST
CMs	0.131	0.106	0.130	0.099
MHs	0.075	0.079	0.130	0.149
CHs	0.131	0.159	0.084	0.115
MOFs	0.150	0.140	0.148	0.131

Finally, using the weighted best and worst values for each criterion, the Euclidean distances and the performance scores were calculated, and the resulting ranking of alternatives are shown in Table 4.

Table 4: Assessment of alternatives

	E_i^+	E_i^-	P_i	Rank
CMs	0.078	0.078	0.500	3
MHs	0.111	0.068	0.379	4
CHs	0.075	0.099	0.570	2
MOFs	0.027	0.120	0.818	1

Based on physical (SA, SC) and chemical (DT, ST) characteristics, the best alternative for solid-state hydrogen storage determined from a combination of quantitative and qualitative assessments are metal-organic frameworks, while the worst are metal hydrides. This agrees with the assessments listed in Table 2, where it can be inferred that MOFs are the best alternative based on the most frequent occurrence of the "Excellent" linguistic assessment among the four alternatives. On the other hand, although metal hydrides have one "Excellent" linguistic assessment, the presence of two "Below Satisfactory" assessments have contributed to its least score and subsequent ranking. Thus, the method presented can serve as a framework for objective assessment in similar cases where a numerical assessment or comparison cannot be directly performed.

4. Sensitivity analysis

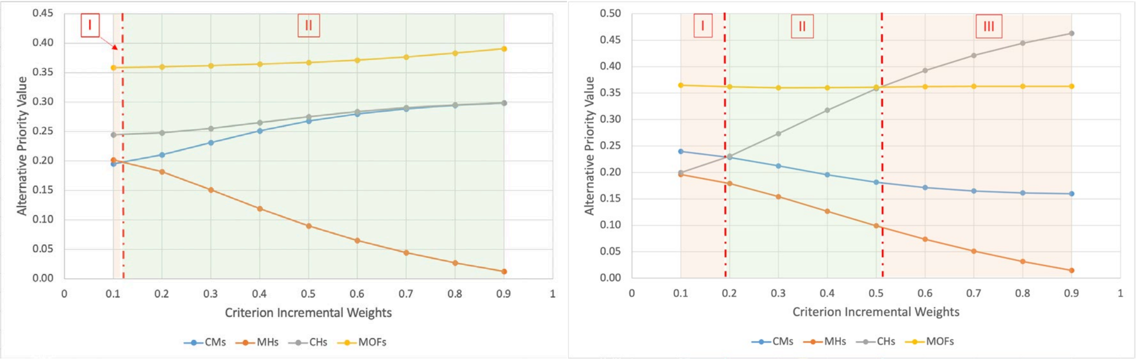
To determine the robustness of the ranking, numerical incremental sensitivity analysis was performed by varying the weights used in Table 3 on each of the criteria such that the balance from unity was spread equally among the remaining criteria. The defuzzified performance scores in Table 4 were normalized into $\widehat{P_i}$ through

$$\widehat{P_i} = \frac{P_i}{\sum_{i=1}^{n} P_i} \tag{8}$$

such that

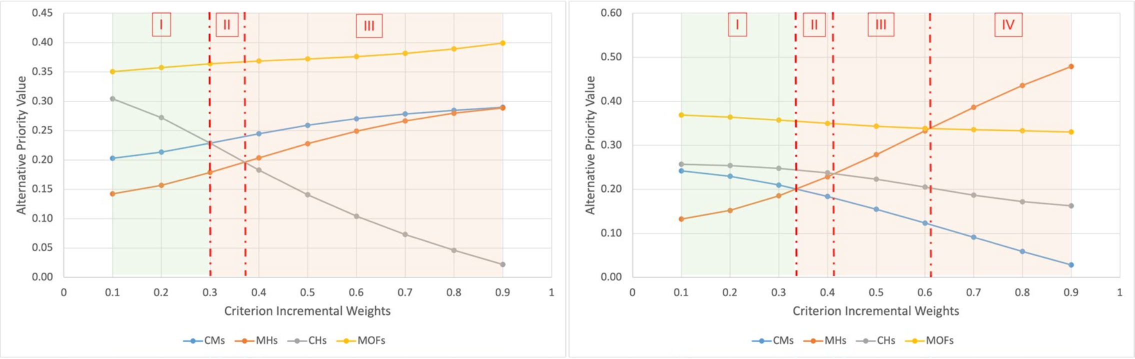
$$\sum_{i=1}^{n} \widehat{P_i} = 1. \tag{9}$$

The resulting sensitivity analysis plots for each of the alternatives are shown in Figure 2. The regions, determined by every intersection of the sensitivity response lines, are labelled I, II, etc., with the region of no rank reversal in reference to the FMCDM solution from the equally weighted criteria assumption highlighted in green. On the other hand, the rank-reversal regions from varying the weights are highlighted in red.



a) b)

Figure 2: Sensitivity Analysis Plot for (a) SA and (b) SC



c)

d)

Figure 2: Sensitivity Analysis Plot for (c) DT and (d) ST

The percent domain values of the FMCDM solution region, $\emptyset_j$, are shown in Table 5 for each of the criterion j.

Table 5: Percent domain of the region of no rank-reversal

Criteria, j	$\emptyset_j$
SA	97.8%
SC	35.6%
DT	22.2%
ST	26.7%

Results indicate that the FMCDM solution ranking is most invariant with respect to SA covering 97.8% of the domain. In contrast, the FMCDM solution ranking is less invariant with respect to SC, DT, and ST. From Figures 2b and 2c, the decreased invariance is attributed to the relatively wider range of $\widehat{P_i}$ values of CHs; the same can be said for MHs from Figure 2d. These agree with the translated qualitative assessment values for CHs and MHs from Table 3, where the largest difference between the maximum and minimum assessment values of 0.380 and of 0.441 can be found for CHs and MHs respectively.

Where the robustness of the ranking is manifested by its invariance across the domain of criterion incremental weight values across all criteria, it intuitively follows that overall ranking robustness is a geometric mean function of the percent domain of the region of no-rank reversal, as shown in Eq(10).

$$R = 1 - \prod_{j=i}^{m} \left(1 - \emptyset_j\right) \tag{10}$$

This novel approach provides a means of quantifying the invariance or robustness of the FMCDM solution. Furthermore, the deviation of R from unity represents the fuzzy nature of the assessment, i.e., as $R \rightarrow 1$, the degree of fuzziness decreases and the robustness of the ranking, in effect, increases. Thus, resolving Eq(10) gives an overall ranking robustness value of 30.1%. This robustness value can be improved by screening specific materials that have tighter assessment virtues or where the ranking of the materials is already apparent even before fuzzy selection, or by narrowing down the domain of weights based on predetermined preferences or constraints.

5. Conclusions

A multi-criteria decision-making technique utilizing spherical fuzzy sets and the technique for order of preference by similarity to ideal solution has been demonstrated in the selection of an optimal class of materials for solid-state hydrogen storage. The demonstration was effective in first defuzzifying qualitative assessments into discreet quantitative values, with the novel approach of utilizing a normal distribution for the degrees of indeterminacy. Based on surface area, sorption capacity, dehydrogenation temperature, and stability, the best alternative are metal-organic frameworks while the worst alternative are metal hydrides. Sensitivity analysis indicates that the FMCDM ranking is most invariant with respect to surface area, while least invariant with respect to desorption temperature. The robustness of the FMCDM solution was 30.1 %, quantified through the second proposed novel approach, underscoring the fuzzy nature of the problem. This method can be tested by attempting to improve the robustness value by screening the alternatives with tighter assessment virtues prior to assessment or by narrowing down the domain of weights.

Nomenclature

μ – degree of membership
η – degree of non-membership
π – degree of indeterminacy
S_n– spherical fuzzy number
S_f– scoring function
β – distance parameter
$\bar{\pi}$ – mean degree of indeterminacy
σ_π – degree of indeterminacy standard deviation
x_{ij} – evaluation value for alternative i and criterion j
$\bar{x}_{ij}$ – normalized evaluation value
n – total number of alternatives
m – total number of criteria
w_{ij} – weighted evaluation value
w_j^+ – weighted best evaluation value
w_j^- – weighted worst evaluation value
E_i^+ – Euclidean distance of alternative alternative i from w_j^+
E_i^- – Euclidean distance of alternative alternative i from w_j^-
P_i – performance score for alternative i
$\widehat{P_i}$ – normalized performance score for alternative i
$\emptyset_j$ – FMCDM solution percent domain for criterion j
R – overall ranking robustness

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