Selection of Phase Change Materials for Latent Heat Storage

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Resumen

Esta investigación tiene como objetivo seleccionar un material de cambio de fase (PCM) que cumplen mejor la solución del almacenamiento de energía térmica entre 200-400 ° C y reducir el costo de producción.

El uso de métodos multicriterios de toma de decisiones (MCMD) para la evaluación fueron proporcionales implementados como COPRAS-G, TOPSIS y VIKOR. La ponderación de los criterios se realizó por el método AHP (proceso analítico jerárquico) y los métodos de entropía. La correlación de los resultados entre los tres métodos de clasificación ha sido desarrollada por el coeficiente de correlación de Spearman. Los resultados ilustran el mejor y la segundo mejor opción para los tres MCDM fueron NaOH y KNO_3. Además, tenía valores de correlación de Spearman entre los métodos excede de 0.714.

***Palabras clave*— Energía solar térmica, almacenamiento de energía térmica por calor latente (LUCES), métodos multicriterios de toma de decisiones, material de cambio de fase (PCM), MCDM, selección de materiales**

Abstract

This research aims to select a phase change material (PCM) which better accomplish the solution of the Thermal Energy Storage between 200–400 °C and reduce the cost of production.

The *Multiple Criteria Decision Making (*MCMD) methods implemented were complex proportional assessment of alternatives with gray relations (COPRAS-G), Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) and Multicriteria Optimization and Compromise Solution (VIKOR) methods. The criteria weighting was performed by compromised weighting method composed of AHP (analytic hierarchy process) and Entropy methods. The correlation of the results between three ranking methods has been developed by the Spearman's rank correlation coefficient. The results illustrated the best and second best choice for the three MCDM were NaOH and KNO_3. Furthermore it had values of Spearman's rank correlation between the methods exceeds of 0,714.

***Index terms*— Solar thermal energy, Latent heat thermal energy storage (LHTES), multi-criteria decision making, phase change material (PCM), methods, MCDM, material selection.**

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1. INTRODUCCIÓN

TES has been a research topic for the last 30 years, but most researchers still feel that one of the weak points of this technology is the material to be used as a storage medium [1-6]. There are mainly three types of TES systems, the sensible heat storage (SHS), the latent heat storage (LHS) and the thermochemical energy storage. SHS can be achieved using solid or liquid media and it involves storing energy in a material without its phase change in the temperature range of the storage process. LHS systems present several advantages in comparison with the other two methods.

- Storing thermal energy at the temperature of process application.

- Storing thermal energy as latent heat which allows higher thermal energy storage capacity per unit weight or material without any change in temperature.

- Storing thermal energy from thermal energy source or electrical energy source when available and use when needed.

Furthermore, they presents economic and environmental benefits

- Storing natural thermal energy for facility heating and cooling needs, which reduce the energy demand and it reduces facilities carbon footprint.

- Storing thermal energy during off demand hours and use during peak demand to save on energy cost and help stabilize grid load.

- Shift of heating and cooling load also reduces peak time stress of heating and cooling equipment that can lead to reduced operating & maintenance cost.

LHS systems with solid-liquid transition or PCM are considered an alternative to SHS systems, especially for solar energy applications in the middle-temperature-range of 200– 400 °C [6, 7]. Molten salt were used as one of the promising LHS medium at middle temperature in solar thermal power systems [8, 9]. Because of the appropriate melting point, low storage unit cost, desirable phase-change temperature range, high heat capacity and energy storage density, nitrates and their binary mixtures as the typical molten salts were used as considerable PCMs. This research tries to resolve the material selection for a PCM which better accomplish the solution of the TES between 200–400 °C.

The selection of the most appropriate material for a particular purpose is a crucial component for the design and development of products. Materials selection has become an important source at engineering processes because of economic, technological, environmental parameters. The objectives and criteria in the material selection process are observed to be often in conflicts, such as desired properties, operating environment, production process, cost, market value, availability of supplying sources and product performance [10, 11].

The application of multi criteria decision making methods (MCDM) for material selection has been conducted in many applications. In 2006, Shanian and Savadogo [12] established a material selection model based on the concept of multiple attribute decision making. In 2008, Ho [13] made a review of the applications of the AHP model integrated with other techniques. In 2014, Anojkumar et al. [14] made a Comparative analysis of MCDM methods for pipe material selection in sugar industry.

Many researches about applications of MCDM have been developed in the energy storage field. In 2009, Bartin et al. [15] studied Multicriteria decision making for management of storage energy technologies on renewable hybrid systems-the analytic hierarchy process and the fuzzy logic, which considers five types of storage energy systems (SES) which are analyzed according to six criteria, in order to find the most suitable type of SES to be used in the environment and costs scenarios. In 2010, Cavallaro [16] developed Fuzzy TOPSIS approach for assessing thermal-energy storage in concentrated solar power (CSP) systems. In this research, a fuzzy logic methodology is used to compare different heat transfer fluids between 400–500 °C in a CSP based on its benefits and costs, in order to investigate the feasibility of employing a molten salt. Fernández et al [17] presented the selection of materials with potential in sensible thermal energy storage in the range of temperatures of 150–200 °C by the CES Selector software. Additionally, in 2013, Khare et al [18] studied Selection of materials for high temperature sensible energy storage. In this research a materials selection software package Granta Design's CES Selector was used to evaluate sensible heat storage between 500–750 °C. However, a study related to the selection of LHS material for TES between 200–400 °C has not been accomplished yet.

In this study has been developed three preference ranking- based MCDM methods, i.e. COPRAS-G, TOPSIS and VIKOR for accurate ranking of the alternative materials for PCMs. The compromised weights have been performed by AHP and Entropy methods. The Spearman's rank correlation has been used to quantify the strength of linear relationship between the results. All the methods have been extensively studied and refined in several articles [19-26]. A more extensive explanation of these methods can be observed in section 2. For these methods, a list of all the possible choices from the best to the worst suitable materials has been obtained taking in consideration different material selection criteria.

This paper is organized as follows: Section 2 Materials and Methods, which describes the definition of the decision making problem, and the MCDM and Spearman's rank correlation, used in this study, Section 3 presents the results of the different MCDM, Section 4 develops the discussion and Section 5 presents the conclusions of this study.

2. MATERIALS AND METHODS

2.1. Definition of the decision making problem

Comparing candidate materials, ranking and choosing the best material are one of most important stages in material selection process. MCDM are analytical tools employed to judge the best alternative of a set of possibilities and easy to adapt for different applications. The MCDM methods can be broadly divided into two categories, as (i) multi-objective decision-making (MODM) and (ii) multi-attribute decision-making (MADM) [27]. There are also several methods in each one of the categories mentioned above. Priority-based, outranking, preferential ranking, distance-based and mixed methods are some of the popular MCDM methods to evaluate and select the most suitable materials for diverse engineering applications [28]. In most MCDM methods a certain weight is assigned to each individual property of the material (which depends on its importance for the application) [27, 28]. Furthermore, efforts need to be extended to identify those criteria that influence a given engineering application to eliminate unsuitable alternatives and select the most appropriate choice using simple and logical method (5), (6). The proper choice of these materials depends on factors such as their physical and thermochemical properties, as well as the type of heat transfer fluid and heat exchanger design. The basic requirements imposed upon LHS materials have been formulated in [5, 9, 29]. These materials should possess following properties:

- The demanded melting temperature, which allows the storage unit to work in a desirable range of working temperatures;
- High specific thermal capacity, heat of fusion and low density to provide the minimum sizes of the HSU.
- Congruent melting: PCMs should keep stoichiometric composition in solid and liquid conditions. Otherwise, distinction in density of the liquid and solid phase, appeared at fusion, will lead to separation of phases, and will change stoichiometric composition of the molten salt;
- Reliable convertibility/ Low grade of decomposition at repeated phase transformations;
- High thermal conductivity to provide the minimum temperature gradients demanded for charging and discharging of the TES unit.
- The minimum change in volume at transition from one phase to another, which allow us to use simple forms of containers and heat exchangers.
- Insignificant overcooling during hardening.
- Chemical stability to provide demanded life time of the TES unit;
- Compatibility with constructional materials to avoid corrosion;
- They must not be toxic or a little toxic;
- Flame and fire safety;
- Availability and low cost.

Fig. 1 illustrates the scheme of a commercial PCM. In order to meet all these requirements, the most important properties are the heat of fusion () and specific heat (). High values are desired to keep the maximum quantity of energy and the minimum size of the HSU. High thermal conductivity () to provide the minimum temperature gradients is required to charge and discharge HSU. Low costs () are desired to provide a competitive advantage among manufacturers. The demanded melting temperature () provides operating the storage unit in a desirable interval of working temperatures. Density (ρ) is important to reduce the downsize of the HSU.

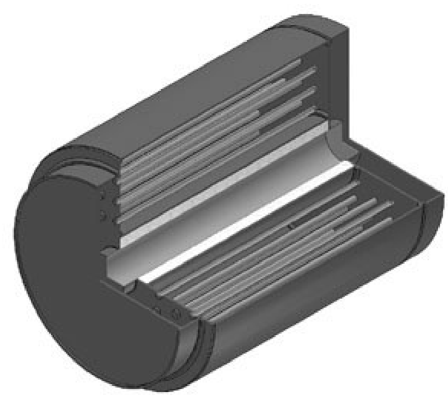

Figure 1: Schema of a TES unit that uses PCM as the thermal storage media and employs the high temperature heat pipes to transfer heat from receiver to PCM to an engine

Seven alternatives for a PCM were taken into consideration: $NaNO_3$, KNO_3, NaOH, KOH, $ZnCl_2$, $NaNO_3/KNO_3$ (0,5/0,5), $ZnCl_2/KCl$ (0,319/0,681). The properties of the alternatives with their quantitative data are given in Table I and their average values were used.

Table 1: Material properties for a PCM (2)-(13).

Material	(A) Heat of fusion, $[\frac{kJ}{kg}]$ (λ)	(B) Specific Heat $[\frac{J}{g \cdot °C}]$ (C_p)	(C) Thermal conductivity $[\frac{W}{m \cdot K}]$ (k)	(D) Cost $[\frac{\$}{kg}]$ (C)	(E) Melting Temp. [°C] (Tm)	(F) Density, $[\frac{kg}{m^3}]$ (ρ)
(1) $NaNO_3$	172	1,82	0,5	0,53	310	2260
(2) KNO_3	266	1,22	0,5	0,78	330	2110
(3) NaOH	165	2,08	0,92	0,34	318	2100
(4) KOH	149,7	1,47	0,5	1,05	380	2044
(5) $ZnCl_2$	75	0,74	0,5	0,9	280	2907
(6) $NaNO_3/KNO_3$ (0,5/0,5)	100,7	1,35	0,56	0,64	220	1920
(7) $ZnCl_2$/KCl (0,319/0,681)	198	0,67	0,8	0,59	235	2480

2.2. Multi-criteria decision making methods

2.2.1 Criteria weighting

The criteria weights are calculated using a compromised weighting method, where the AHP and Entropy methods were combined, in order to take into account the subjective and objective weights of the criteria and to obtain more reasonable weight coefficients. The synthesis weight for the jth criteria is:

$$\boldsymbol{w_j = \frac{\alpha_j x \beta_j}{\sum_{j=1}^{n} \alpha_j x \beta_j} \quad j = 1, \dots, n} \qquad (1)$$

where α_j is the weight of jth criteria obtained via AHP method, and β_j is the weight of jth criteria obtained through Entropy method.

2.2.2 Analytic hierarchy process (AHP)

The AHP method is a well-structured technique for organizing and analyzing complex decisions based on mathematics and psychology. It was developed by Saaty [19] in the 1970s to model subjective decision-making processes based on multiple criteria in a hierarchical system. It has been extensively studied and refined since then.

In order to identify the importance of every alternative in an application, each alternative has been assigned a value. The ranking is composed by three levels: 1). general objective, b). criteria for every alternative, c). alternatives to regard [19].

The weight of criteria regard to others is set in this section. To quantify each coefficient requires experience and knowledge of the application [20]. Saaty [19] classified the importance of parameters showed in Table II. The relative importance of two criteria is rated using a scale with the digits 1, 3, 5, 7 and 9, where 1 denotes "equally important", 3 for "slightly more important", 5 for "strongly more important", 7 for "demonstrably more important" and 9 for "absolutely more important". The values 2, 4, 6 and 8 are applied to differentiate slightly differing judgements. The comparison among n criteria is summarized in matrix A (***nxn***), and the global arrange is expressed in equation (2).

$$\boldsymbol{A = \begin{pmatrix} a_{11} & \cdots & a_{1n} \\ \vdots & \ddots & \vdots \\ a_{n1} & \cdots & a_{nn} \end{pmatrix} \qquad a_{ii} = 1, a_{ji} = \frac{1}{a_{ij}}, a_{ij} \neq 0} \quad (2)$$

Afterwards, from matrix ***A*** it is determined the relative priority among properties. The eigenvector ***w*** is the weight importance, and it corresponds with the largest eigenvector (λ_{max}):

$$\boldsymbol{(A - \lambda_{max})w = 0} \qquad (3)$$

The consistency of the results is summarized by the pairwise comparison of alternatives. Matrix ***A*** can be ranked as 1 and λ_{max} = n [20].

In order to ensure the consistency of the subjective perception and the accuracy of the results, it is necessary to distinguish the importance of alternatives among them. In equations (4) and (5) is shown the consistency indexes required to validate the results.

$$\boldsymbol{CI = \frac{(\lambda_{max} - n)}{n-1}} \qquad (4)$$

$$\boldsymbol{CR = \frac{CI}{RI}} \qquad (5)$$

Where:

n : Number of selection criteria.

RI: Random index.

CI: Consistency index.

CR: Consistency relationship.

λ_{max}***(A):*** Largest eigenvalue.

The ***CR*** should be under 0.1 for a reliable result. Otherwise, the importance coefficient (1-9) has to be set again and ***CR*** recalculated [19]. The ***IR***. is determined for different size matrixes, and its value is 1.32 for a 7x6 matrix.

2.2.3 Entropy method

Entropy method indicates that a broad distribution represents more uncertainty than the sharply peaked one [21]. Equation (6) shows the decision matrix A of multi-criteria problem with m alternatives and n criteria:

$$A = \begin{array}{c} A_1 \\ A_2 \\ \vdots \\ A_m \end{array} \begin{bmatrix} x_{11} & x_{12} & \cdots & x_{1n} \\ x_{21} & x_{22} & \ddots & x_{2n} \\ \vdots & \vdots & \cdots & \vdots \\ x_{n1} & x_{n2} & \cdots & x_{nn} \end{bmatrix};\ x_1, x_2, \dots x_n; \quad (6)$$

where x_{ij} $(i = 1, 2, \dots, m;\ j = 1, 2, \dots, n)$ is the performance value of the ***ith*** alternative to the ***jth*** criteria.

The normalized decision matrix P_{ij} is calculated [21], in order to determine the weights by the Entropy method.

$$P_{ij} = \frac{x_{ij}}{\sqrt{\sum_{i=1}^{m} x_{ij}^2}} \quad (7)$$

The Entropy value E_j of ***jth*** criteria can be obtained as:

$$E_j = -k \sum_{i=1}^{m} P_{ij}\, ln(P_{ij}) \qquad j = 1, 2, \dots, n \quad (8)$$

where $k = \frac{1}{ln\, m}$ is a constant that guarantees $0 \le Ej \le 1$, and m is the number of alternatives. The divergence degree (d_j) of the average information contained by each criterion can be obtained from Eq. (9):

$$d_j = |1 - E_j| \quad (9)$$

Thus, the weight of Entropy of ***jth*** criteria can be defined as:

$$\beta_j = \frac{d_j}{\sum_{j=1}^{n} d_j} \quad (10)$$

2.2.4. COPRAS-G method

COPRAS-G [22] is a MCDM method that applies gray numbers to evaluate several alternatives of an engineering applications. The gray numbers are a section of the gray theory to confront insufficient or incomplete information [23]. White number, gray number and black number are the three classifications to distinguish the uncertainty level of information.

The uncertainty level can be expressed by three numbers: white, gray and black.

Let the number $\otimes X = [\underline{x}, \overline{x}] = \{x | \underline{x} \le x \le \overline{x}\}$ and $x \epsilon R$, where $\otimes X$ has two real numbers, $\underline{x}$ (the lower limit of $\otimes X$) and $\overline{x}$ (the upper limit of $\otimes X$) is defined as follows:

a) White number: if $\underline{x} = \overline{x}$, then $\otimes X$ has the complete information.

b) Gray number: $\otimes X = [\underline{x}, \overline{x}]$ means insufficient and uncertain information.

c) Black number: if $\underline{x} \to \infty$ and $\overline{x} \to \infty$,, then $\otimes X$ has no meaningful information.

The COPRAS-G method uses a stepwise ranking and evaluating procedure of the alternatives in terms of significance and utility degree. The procedure of applying COPRAS-G method is formulated by the following steps [22, 23]:

Step 1: Selection of a set of the most important criteria, describing the alternatives and developing the initial decision matrix, $\otimes X$.

$$\otimes X \begin{pmatrix} \otimes x_{11} & \otimes x_{12} & \cdots & \otimes x_{1n} \\ \otimes x_{21} & \otimes x_{22} & \ddots & \otimes x_{2n} \\ \vdots & \vdots & \cdots & \vdots \\ \otimes x_{m1} & \otimes x_{m2} & \cdots & \otimes x_{mn} \end{pmatrix} = \begin{pmatrix} (x_{11}, b_{11}) & (x_{12}, b_{12}) & \cdots & (x_{1n}, b_{1n}) \\ (x_{21}, b_{21}) & (x_{22}, b_{22}) & \ddots & (x_{2n}, b_{2n}) \\ \vdots & \vdots & \cdots & \vdots \\ (x_{m1}, b_{m1}) & (x_{m1}, b_{m1}) & \cdots & (x_{mn}, b_{mn}) \end{pmatrix} \quad (11)$$

where $\otimes x_{ij}$ is the interval performance value of ***ith*** alternative on ***jth*** criterion. The value of $\otimes x_{ij}$ is determined by x_{ij} (the smallest value or lower limit) and b_{ij} (the biggest value or upper limit).

Step 3: Normalization of the decision matrix, $\otimes X$ using the following equations. Eq. (12) is applied for x_{ij} or lower limit values, whereas, Eq. (13) is used for b_{ij} or upper limit values.

$$\otimes \overline{X} = |\overline{x}_{ij}|_{mxn} = \frac{2x_{ij}}{\left[\sum_{j=1}^{n} x_{ij} + \sum_{j=1}^{n} b_{ij}\right]} \quad (12)$$

$$\otimes \bar{X} = \left|\bar{b}_{ij}\right|_{mxn} = \frac{2b_{ij}}{\left[\sum_{j=1}^{n} x_{ij} + \sum_{j=1}^{n} b_{ij}\right]} \quad (13)$$

Step 4: Weight calculation of each criterion.

Step 5: Determination of weighted normalized decision matrix, $\otimes \bar{X}$ by mean of the equations (14) and (15).

$$\otimes \bar{\bar{X}} = \left|\bar{\bar{x}}_{ij}\right|_{mxn} = \bar{x}_{ij} \times w_j \ (i = 1, 2, \dots, m; j = 1, 2, \dots, n) \quad (14)$$

$$\otimes \bar{\bar{X}} = \left|\bar{\bar{b}}_{ij}\right|_{mxn} = \bar{b}_{ij} \times w_j \quad (15)$$

Step 6: The weighted mean normalized sums are calculated for both the beneficial attributes P_i based on equation (16) and non-beneficial attributes R_i based on equation (17) for all the alternatives.

$$P_i = \frac{1}{2}\sum_{j=1}^{k}(\bar{\bar{x}}_{ij} + \bar{\bar{b}}_{ij}) \quad (16)$$

$$R_i = \frac{1}{2}\sum_{j=k+1}^{n}(\bar{\bar{x}}_{ij} + \bar{\bar{b}}_{ij}) \quad (17)$$

Step 7: Determination of the minimum value of R_i .

$$R_{min} = Min\, R_i \ \ (i = 1, 2, \dots, m) \quad (18)$$

Step 8: Determination of the relative significances or priorities of the alternatives. The priorities of the candidate alternatives are calculated on the basis of Q_i with equation (19). The greater the value of Q_i, the higher is the priority of the alternative. The alternative with the highest relative significance value (Q_{max}) is the best choice among the feasible candidates.

$$Q_i = P_i + \frac{R_{min}\sum_{i=1}^{m} R_i}{R_i \sum_{i=1}^{m}(R_{min}/R_i)} \quad (19)$$

Step 9: Determination of the maximum relative significance value.

$$Q_{max} = Max Q_i \quad (i = 1, 2, \dots\dots, m) \quad (20)$$

Step 10: Calculation of the quantitative utility (U_i) for ***ith*** alternative through the equation (21). The ranking is set by the Q_i.

$$U_i = \left[\frac{Q_i}{Q_{max}}\right] x100\% \quad (29)$$

With the increase or decrease in the value of the relative significance for an alternative, it is observed that its degree of utility also increases or decreases. These utility values of the candidate alternatives range from 0 % to 100 %. The best alternative is assigned according to the maximum value of 100%.

2.2.5. TOPSIS method

The basic idea of TOPSIS is that the best decision should be made to be closest to the ideal and farthest from the non-ideal [24]. Such ideal and negative-ideal solutions are computed by considering the various alternatives. The highest percentage corresponds to the best alternative.

The TOPSIS approach is structured by the following procedure [24]:

Step 1: Normalize the decision matrix n_{ij} by its performance using equation 22.

$$n_{ij} = \frac{x_{ij}}{\sqrt{\sum_{i=1}^{n} x_{ij}^2}} \quad (22)$$

Where x_{ij} is the performance measure of ***jth*** criterion respect to ***ith*** alternative.

Step 2: Synchronization of the weight w_j and the normalized matrix , see equation (23).

$$V_{ij} = n_{ij} \cdot w_j \quad (i = 1, 2, \dots, m;\ j = 1, 2, \dots, m) \quad (23)$$

Step 3: The ideal solutions (V^+) and nadir solutions (V^-) are determined using (24) and (25):

$$\{V_1^+, V_2^+, \dots, V_n^+\} = \{(max_i V_{ij} | j \in K), (min_i V_{ij} | j \in K')\} \ \{i = 1, 2, \dots, m\} \quad (24)$$

$$\{V_1^-, V_2^-, \dots, V_n^-\} = \{(min_i V_{ij} | j \in K), (max_i V_{ij} | j \in K')\} \ \{i = 1, 2, \dots, m\} \quad (25)$$

Where K and K' are the index set of benefit criteria and the index set of cost criteria, respectively.

Step 4: The distance between the ideal and nadir solution is quantified. The two Euclidean distances for each alternative are computed as given by equations (26) y (27):

$$S_i^+ = \sqrt{\sum_{j=1}^{n}(V_{ij} - V_j^+)^2} \quad i = 1, 2, \dots, n; \quad i = 1, 2, \dots, n \quad (26)$$

$$S_i^- = \sqrt{\sum_{j=1}^{n}(V_{ij} - V_j^-)^2} \quad i = 1,2,\dots,n; \qquad i = 1,2,\dots,n \tag{27}$$

Step 5: The relative closeness (C_i) is computed by equation (28).

$$C_i = \frac{S_i^-}{S_i^- + S_i^-} \quad i = 1,2,\dots,m; \;\; 0 \le C_i \le 1 \tag{28}$$

The highest C_i coefficients correspond to the best alternatives.

2.2.6. VIKOR method

The VIKOR method was originally developed to solve decision problems with conflicting and different criteria, assuming that compromise is acceptable for conflict resolution, the decision maker wants a solution that is the closest to the ideal, and the alternatives are evaluated according to all established criteria. The VIKOR method considers the closeness to the ideal solution in order to rank the alternatives [25]. The value closest to zero corresponds to the best alternative.

Step 1: Select the maximum magnitude $(x_{ij})_{max}$ and minimum magnitude $(x_{ij})_{min}$ values of all criteria are determined from decision matrix.

Step 2: The values of E_i and F_i are calculated from Eqs. (29) and (30), respectively.

$$E_i = \sum_{j=1}^{n} w_j \frac{[(x_{ij})_{max} - (x_{ij})]}{[(x_{ij})_{max} - (x_{ij})_{min}]} \tag{29}$$

$$F_i = Max^n of \left\{ w_j \frac{[(x_{ij})_{max} - (x_{ij})]}{[(x_{ij})_{max} - (x_{ij})_{min}]} \right\} \quad j = 1,2,\dots,n \tag{30}$$

Where w_j are the weights

Step 3: values of P_i are calculated by equation (31):

$$P_i = v\left(\frac{E_i - E_{i-min}}{E_{i-max} - E_{i-min}}\right) + (1 - v)\left(\frac{F_i - F_{i-min}}{F_{i-max} - F_{i-min}}\right) \tag{31}$$

Where

- $E_{i\text{-}max}$ designates the maximum value of E_i.
- $E_{i\text{-}min}$ designates the minimum value of E_i.
- $F_{i\text{-}max}$ is the maximum value of F_i.
- $F_{i\text{-}min}$ is the minimum value of F_i.
- v is used as the weight of the strategy of 'the majority of criteria' (or "the maximum group utility"). The value of v is usually taken as 0,5. However, it can take any value from 0 to 1 which define the strategy.

Step 4: Rank the results according to P_i, E_i and F_i, in different cells.

The best alternative is determined as the one with the minimum value of P_i in the P ranking. The alternative (x') with the minimum P value is proposed as compromise solution for given criteria weights, if conditions (1) and (2) are satisfied [25]:

Condition 1. "Acceptable advantage" $P(x'')-P(x') \ge (\frac{1}{1-m})$, where x'' is the second-best alternative in the ranking made according to P and m is the number of alternatives.

Condition 2. "Acceptable stability in decision making": The alternative x' must also be the best in the ranking made according to E and/or F. This compromise solution is stable within a decision-making process, which could be: "voting by majority rule" (when $v > 0,5$ is needed) or "by consensus" (when $v \approx 0,5$), or "with veto" (when $v > 0,5$).

If one of the conditions is not fulfilled, one of the following alternatives can be adopted: Alternatives x' and x'' if only C2 is not satisfied.

- Alternatives $x', x'', \dots, x^{(k)}$ if condition not satisfied; $x^{(k)}$ is determined by the relation $P(x^{(k)})- P(x') < (1/(m-1))$ the positions of these alternatives are "in closeness"

2.2.7. Spearman's rank correlation coefficient

The Spearman's rank correlation coefficient measures the relation among nonlinear datasets. Its purpose is to quantify the strength of linear relationship between two variables. If there are no repeated data values, a perfect Spearman correlation of +1 or −1 occurs when each of the variables is a perfect monotone function of the other [26]. The Spearman's rank correlation is computed by equation (32).

$$R_s = 1 - \frac{6\sum d_i^2}{n(n^2-1)} \tag{32}$$

Where is Spearman's rank coefficient, is the difference between ranks of each case and is thenumber of pairs of values

3. RESULTS

The weight of each criteria have been computed by the AHP method and Entropy method regarding its importance for a PCM. After the determination of the weights, they have been applied to the COPRAS-G, TOPSIS and VIKOR methods. The different steps involved in these methods were discussed above. The results have been compared by means of Spearman's rank correlation coefficient in order to determine their convergence and sensibility to rank the best solutions.

3.1. Criteria weighting

The comparison among properties of every alternative are in Table 1. The properties identification appears under the name of each property as ***(λ), (C_p), (k), (C), (T_m)*** and ***(ρ)***. The weight of each alternative was assigned according to the AHP and Entropy methods. The criteria weighting was firstly performed by the AHP method. After the decision hierarchy for the problem was designed, the criteria was compared pairwise based on the experience of the authors using the scale given in section 2.1.1. In Table 2 shows the scale of AHP method.

Table 1: Scale of relative importance

Definition	Intensity of importance
Equal importance	1
Moderate importance	3
Strong importance	5
Very strong importance	7
Extreme importance	9
Intermediate importance	2, 4, 6, 8

Table 2: Comparison among criteria for balanced scales AHP

(λ)	(C_p)	(k)	(C)	(T_m)	(ρ)
1	3	5	5	7	9
0,333	1	3	3	5	7
0,2	0,333	1	1	3	5
0,2	0,333	1	1	3	5
0,143	0,2	0,333	0,333	1	3
0,111	0,143	0,2	0,2	0,333	1

Table 3: normalized decision matrix for entropy method

Material	(λ)	(C_p)	(k)	(C)	(T_m)	(ρ)
1	0,380	0,485	0,299	0,276	0,390	0,374
2	0,588	0,325	0,299	0,407	0,415	0,350
3	0,364	0,554	0,550	0,177	0,400	0,348
4	0,331	0,391	0,299	0,548	0,478	0,339
5	0,166	0,197	0,299	0,469	0,352	0,482
6	0,222	0,359	0,335	0,334	0,277	0,318
7	0,437	0,178	0,478	0,308	0,295	0,411

Table 4: Criteria weighting by the AHP ($α_j$) and balanced scales entropy ($β_j$), methods and compromised weighting (w_j)

	(λ)	(C_p)	(k)	(C)	(T_m)	(ρ)
$α_j$	0,461	0,240	0,109	0,109	0,051	0,028
$β_j$	0,146	0,146	0,173	0,157	0,187	0,192
w_j	0,440	0,228	0,123	0,112	0,063	0,035

In Table 3 is illustrated the decision matrix generated for a PCM which better accomplish the solution of the TES between 200–400 °C. The most important criteria to generate the matrix was considered (***λ***); moderate more important was taken (***C_p***); strongly more important was considered (***k***); (***C***); very strongly more important was considered (***T_m***); extremely more important was taken (***ρ***). The results are consistent due to the value of the consistency index (***CI*** = 0,052) and the consistency ratio (***CR***=0,041) which are lower than the limit 0,1. At the final step, the compromised weights of the criteria (***w_j***) were calculated using the Eq. (1). The normalized decision matrix for the entropy method in appears in Table 4 .In Table 5, the weight coefficient of every criterion was determined based in results of AHP and Entropy methods. On one hand, the most representative values are (***λ***) 44,0 % and taken (***k***) 22,8 %. On the other hand, less than 34 % of the overall weight is distributed in (***C_p***), (***C***), (***T_m***) and (***ρ***).

3.2. COPRAS-G

The related decision matrix is first developed from the gray numbers applied in COPRAS-G as illustrated in Table 5. Equations 12 and 13 allow to develop decision matrix with normalized weights, as is given in Table 6. Later, the normalized matrix and the weight are compared by means of equations 14 y 15. Table 7 exhibits the priority values (Qi) and quantitative utility (Ui) values for the candidate alternatives of the PCM, which were calculated using equations (19) and (21) respectively. Table 7 also shows the ranking of the alternative material as 2-3-1-7-4-6-5. NaOH and KNO_3, obtain the first and second ranks respectively.

Table 5: decision matrix of COPRAS-G method

Mat.	(λ)		(C_p)		(k)		(C)		(T_m)		(ρ)	
1	154	189	1,63	2,00	0,45	0,55	0,477	0,583	279	341	2034	2486
2	239	292	1,09	1,34	0,45	0,55	0,702	0,858	297	363	1899	2321
3	148	181	1,87	2,28	0,828	1,012	0,306	0,374	286	349	1890	2310
4	134	164	1,32	1,61	0,45	0,55	0,945	1,155	342	418	1839	2248
5	67,5	82,5	0,66	0,814	0,45	0,55	0,81	0,99	252	308	2616	3197
6	90,63	110	1,21	1,48	0,504	0,616	0,576	0,704	198	242	1728	2112
7	178	217	0,60	0,737	0,72	0,88	0,531	0,649	211	258	2232	2728

Table 6: Normalized matrix made of gray numbers

Mat.	(λ)		(C_p)		(k)		(C)		(T_m)		(ρ)	
1	0,06	0,07	0,04	0,05	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01
2	0,09	0,11	0,03	0,03	0,01	0,01	0,01	0,02	0,01	0,01	0,01	0,01
3	0,05	0,07	0,05	0,05	0,02	0,03	0,01	0,01	0,01	0,01	0,01	0,01
4	0,05	0,06	0,03	0,04	0,01	0,02	0,02	0,03	0,01	0,01	0,01	0,01
5	0,03	0,03	0,02	0,02	0,01	0,02	0,02	0,02	0,01	0,01	0,01	0,01
6	0,03	0,04	0,03	0,04	0,01	0,02	0,01	0,01	0,01	0,01	0,01	0,01
7	0,07	0,08	0,01	0,02	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01

Table 7: Pi, Ri, Qi and Ui values

Material	Pi	Ri	Qi	Ui	Rank
1	0,134	0,015	0,153	83,823	3
2	0,156	0,019	0,172	94,076	2
3	0,157	0,011	0,183	100,000	1
4	0,122	0,023	0,135	73,938	4
5	0,078	0,023	0,090	49,510	7
6	0,098	0,016	0,117	64,076	6
7	0,115	0,017	0,133	72,745	5

3.3. TOPSIS

The decision matrix given in Table 1 was normalized using equation (22) for the application of the TOPSIS method and this was multiplied by the compromised weights obtained. In Table 8 is shown the weighted and normalized decision matrix V_{ij} for the PCM alternatives. The ideal and nadir ideal solutions, determined by equations (24) and (25), are presented in Table 9. The distances from the ideal (S_i^+) and nadir ideal solutions (S_i^-) and the relative closeness to the ideal solution (C_i) are measured using equations (26)–(28). The PCM alternatives could be ranked by the relative degree of approximation.

Table 8: Weighted and normalized decision matrix,

Material	(λ)	(C_p)	(k)	(C)	(T_m)	(ρ)
1	0,167	0,110	0,037	0,031	0,024	0,013
2	0,258	0,074	0,037	0,046	0,026	0,012
3	0,160	0,126	0,068	0,020	0,025	0,012
4	0,145	0,089	0,037	0,061	0,030	0,012
5	0,073	0,045	0,037	0,053	0,022	0,017
6	0,098	0,082	0,041	0,037	0,017	0,011
7	0,192	0,041	0,059	0,034	0,018	0,014

Table 9: The ideal and nadir ideal solutions of TOPSIS method

	(λ)	(C_p)	(k)	(C)	(T_m)	(ρ)
V^+	0,258	0,126	0,068	0,020	0,030	0,011
V^-	0,073	0,041	0,037	0,061	0,017	0,017

Table 10: Computation details for TOPSIS method

Material	S_i^+	S_i^-	C_i	Rank
1	0,098	0,121	0,552	3
2	0,066	0,189	0,741	1
3	0,098	0,133	0,575	2
4	0,130	0,088	0,405	5
5	0,208	0,011	0,050	7
6	0,170	0,054	0,242	6
7	0,110	0,124	0,531	4

The ranking is shown in Table 10. The ranking of the alternative material are 2-3-1-7-4-6-5. For TOPSIS method KNO_3 and NaOH obtain the first and second ranks materials for the PCM. $ZnCl_2$ had the last rank and $NaNO_3/KNO_3$ had the second last rank.

3.4. VIKOR

The values of E_i, F_i and P_i were calculated using equations (29)–(31) as shown in Table 11. The material with the lowest P_i value was given the best rank. According to the ranking of alternatives by the VIKOR method presented in Table 11, the ranking materials for a PCM is 2-3-1-7-4-6-5, which indicates that KNO_3 and NaOH obtain the first and second ranks for the PCM materials. On the other hand, $ZnCl_2$ had the last rank and $NaNO_3/KNO_3$ had the second last rank.

Table 11: Computation details for VIKOR method

Material	E_i	F_i	P_i	Rank
1	0,514	0,216	0,293	3
2	0,352	0,139	0,000	1
3	0,397	0,232	0,201	2
4	0,520	0,268	0,385	5
5	0,842	0,440	1,000	7
6	0,766	0,380	0,824	6
7	0,564	0,228	0,364	4

3.5. SPEARMAN'S CORRELATION COEFFICIENTS

In Table 12 is shown the Spearman's correlation coefficients for a PCM. These represent the mutual correspondence among MCDM methods. The magnitude of this parameter for a PCM exceeds 0,714 for the relation of the results between the methods COPRAS-G, TOPSIS and VIKOR. In case of the magnitude of the parameter between TOPSIS and VIKOR it has a value of 1, which indicates that all the results have the same rank.

Table 12: Spearman's correlation indexes

	TOPSIS	VIKOR
COPRAS	0,714	0,714
TOPSIS	-	1,000

4. DISCUSSION

The MCDM are an important tool to recognize and identify the best alternative in a bunch of several of them. These methods can adapt to different sort of environments and conditions that would affect the final result and that is why these approaches are applied in different areas of science, engineering and management.

In this case, we take advantage of MCDM in order to know the best alternative for a PCM. In Fig. 2 is summarized the overall rank of each MCDM method for the different material alternatives. It has been observed for COPRAS-G, VIKOR, and TOPSIS methods, the best material alternative and second best alternative correspond to NaOH and KNO_3, because they have the highest values for the most important properties for a PCM. The main contribution to the field of this results is to obtain a material for TES with high heat of fusion (***λ***), specific heat ($\boldsymbol{C_p}$) and thermal conductivity (***k***) with the low cost. In contrast, to get all the heat of fusion the operation temperature of the TES should be designed above 310 °C for NaOH and above 330 °C KNO_3. In case of the maximum temperature at service will not pass this value it should choose other compound.

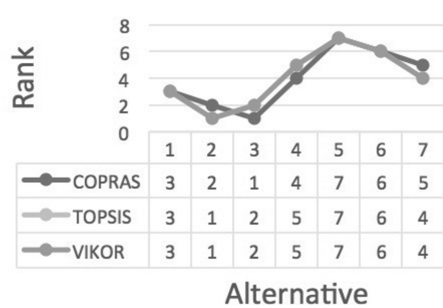

Figure 2: Rank materilas vs. alternative materials for the PCM

Similar properties have been used in the studies of Khare et al [18] in the selection of materials for high temperature sensible energy storage and Fernández et al [17] in the Selection of materials with potential in sensible thermal energy storage between 150–200 °C, which have been taken into account how the most important properties the high heat of fusion (***λ***), specific heat ($\boldsymbol{C_p}$) and thermal conductivity (***k***), with cost (***C***) and density (***ρ***) are the most important properties for materials in TES applications. Moreover, Fernández et al [17] considered the fracture toughness, but this is relevant for the structure which contains PCM and not for the materials of the LHS.

5. CONCLUSIONS

In this paper the material selection problem for a PCM at middle temperature between 200–400 °C for LHS has been solved utilizing a decision model. The model includes the COPRAS-G, VIKOR and TOPSIS methods. Ranking scores which were used to rank the alternative materials were obtained as results of the methods. According to the results of COPRAS, VIKOR and TOPSIS methods, the best and second best choice are NaOH and KNO_3, because they have highest values of the most important criteria for a PCM.

The results show that make a TES with NaOH and KNO_3, could reduce the manufacturing cost with a high heat of fusion (***λ***), specific heat ($\boldsymbol{C_p}$) and thermal conductivity (***k***). This properties should improve the energy efficiency of the TES. In addition, it should take into account that to obtain all the heat of fusion for the TES , the operation temperature should be above 310 °C for NaOH and above 330 °C KNO_3. In case of the maximum temperature at service will not pass this value it should choose other compound.

In conclusion, the MCDM approach is a viable tool in solving the complex material selection decision problems. Spearman's rank correlation coefficient was found to be very useful in assessment of the correlation between three ranking methods. The model which was developed for the material selection for a PCM can be applied on other applications for material selection problems.

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