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Organic syntheses greenness assessment with multicriteria decision analysis

Marek Tobiszewski[a*], Witold Przychodzeń[b], Marta Bystrzanowska[a], Maria J. Milewska[b]

Green chemistry requires the metrics system that are comprehensive by the criteria included and simple in application at the same time. We propose the application of multicriteria decision analysis for comparative assessment of organic synthesis procedures greenness assessment. The assessment is based on 9 criteria (reagent, reaction efficiency, atom economy, temperature, pressure, synthesis time, solvent, catalyst and reactant) for which datapoints are easily extractable from synthesis protocols. The criteria are given weights by the two experts to differentiate their relative importance. Two datasets are created, one of the procedures for benzoic acid synthesis, the second one of procedures for γ-valerolactone synthesis. In both cases the greenest procedure is identified and the remaining ones are ranked according to their greenness. The proposed assessment procedure incorporates more assessment criteria than product/waster ratio mass based metric and is much less tedious than the application of life-cycle assessment.

Introduction

Green chemistry with its 12 principles is well recognized in chemical laboratories and industry[1]. The 12 principles deal with many aspects of chemical process, such as effectiveness of substrates utilization, benignness of all chemicals included in the process, energy requirements, auxiliary materials consumption, safety of operator[2]. This variety of considerations makes the greenness assessment of chemical processes complex. Authors of contributions dealing with chemical processes tend to overuse the phrase “green” as their statements sometimes are based on single criterion or no criteria at all. This shows that the assessment tools should be able to deal with multidimensionality of greenness of chemical processes[3].

The most widely accepted greenness metrics applied for chemical reactions are E(nvironmental) Factors[4,5]. E Factor is calculated by dividing mass of waste generated during reaction by the mass of reaction product, typically expressed in kg kg-1. Another widely accepted metrics is atom economy that quantifies the mass of substrates that end up in the final product, expressed in per cents[6]. Another mass-based metric is Process Mass Intensity (PMI) that quantifies the total mass of all materials per mass of product[7], expressed in kg kg-1. EcoScale[8] is the metric system that considers another aspects than material utilization efficiency. It is based on penalty points that are subtracted from the base 100 points. The penalty point are given for poor yield, expensive or dangerous reagents, non-standard technical setup, deviations from room temperature or problematic purification systems.

There are many other metric systems applicable to assess synthesis reactions greenness[9]. The metrics have certain limitations. The most of the existing greenness metrics are referring to single criterion only (all waste and product mass related metrics) or the differences between the methodologies are hardly noticeable. Life-cycling approach seems to be too complex to be routinely applied during assessment of procedures greenness[10]. There are also scoring systems that have been proposed for greenness assessment. Green chemistry metrics (GCM)[11] is applied for the assessment of products or processes. GCM refers to the 12 principles of green chemistry and is based on direct comparison between available chemicals or processes. For each principle the respective score is assigned according to the preference giving easily comparable principle scores and the sum of scores for all 12 principles allows to rank the alternatives. Another assessment tool based on scoring according to the 12 principles is iSUSTAIN™ toolkit, developed for educational purposes.[12] The scores for each of categories are expressed with 0-100 scale and are plotted on spider diagram, what allows for ease of alternatives performance comparison in different aspects. The educational metrics also based on spider diagram is the Green star tool.[13] In very simplistic way it refers to the principles of green chemistry, allowing students to familiarize students with its concepts.

Another possibility is the application of multicriteria decision analysis (MCDA)[14]. This is the group of tools that allow to rank

the alternatives according to given criteria[15]. They are applied in decision making processes within financial, management, including environmental management, risk assessment areas. These tools have the advantages of giving possibility to deal with decision problem in systematic, formalized way and applying many assessment criteria that are often contradictory to each other. MCDA tools are flexible as they allow to define the criteria according to the given goal and differentiate between criteria significance by assigning to them weights[16]. The output is easy to be interpreted and the assessment procedure can be usually performed with the dedicated software. The applications of MCDA in chemical sciences are rather scarce[17]. The applications in green chemistry include assessment of ionic liquids[18], deep eutectic solvents[19], traditional solvents[20], nanoparticles[21] and analytical procedures[22]. MCDA has high potential to be applied as comparative greenness assessment tool for chemical synthesis reactions.

Therefore, the aim of the study is to show the applicability of MCDA as the tool for the greenness assessment of organic synthesis processes. The selection of relevant criteria and assigning of their weights will be presented. MCDA advantages and limitations will be discussed and compared with other tools applied in synthesis greenness assessment.

Materials and Methods

TOPSIS general procedure

For the purpose of organic synthesis procedures evaluations, the TOPSIS algorithm (The Technique for Order of Preference by Similarity to Ideal Solution) has been chosen (due to ease of interpretation and relatively simple mechanism). Its algorithm was developed by Hwang and Yoon[23], and the aim is to select the best option among all given based on obtained ranking of available alternatives. The most beneficial alternative is characterised by the shortest distance from the positive ideal solution and, at the same time, the farthest distance from the negative ideal solution. This mathematical model allows for combination of different (often contradictory) criteria into a single score gathered in ranking of available alternatives. The ranking is defined by the values of similarity to ideal solution, that ranged between 0 and 1 (values for each of the alternatives). The value 0 is assigned to completely non-ideal alternative (the worst values for all criteria), whereas the value of 1 identifies the best values for all criteria (the ideal solution).

Typically, the input data for TOPSIS analysis consists of the matrix of n alternatives described by m criteria. The procedure can be described in following steps:

- Construction of normalised matrix

$$\boldsymbol{r_{ij} = x_{ij} \div \sqrt{\sum x_{ij}^2}, i = 1, 2, \dots, m \wedge j = 1, 2, \dots, n} \quad (1)$$

Where x_{ij} and r_{ij} are original and normalized scores in decision matrix, respectively.

- Construction of the weighted normalised decision matrix

$$\boldsymbol{v_{ij} = r_{ij} \times w_j, i = 1, 2, \dots, m \wedge j = 1, 2, .., n} \quad (2)$$

Where w_j is the weight of the criterion j and the sum of all weights must equal to 1 - $\boldsymbol{\sum_{j=1}^{n} w_j = 1}$

- Determination of positive ideal (A^*) and negative ideal (A^-) solutions

$$A^* = \{(\boldsymbol{max_i v_{ij} \vee j \in C_b}), (\boldsymbol{min_i v_{ij} \vee j \in C_c})\} = \{\boldsymbol{v_i^* \vee j = 1, 2, \dots, m}\} \quad (3)$$

$$A^- = \{(\boldsymbol{min_i v_{ij} \vee j \in C_b}), (\boldsymbol{max_i v_{ij} \vee j \in C_c})\} = \{\boldsymbol{v_j^* \vee j = 1, 2, \dots, m}\} \quad (4)$$

- Calculation of the separation scores for each of the alternatives

$$\boldsymbol{S_i^* = \sqrt{\sum_{j=1}^{m} (v_{ij} - v_j^*)^2}\, j = 1, 2, \dots, m} \quad (5)$$

$$\boldsymbol{S_i^- = \sqrt{\sum_{j=1}^{m} (v_{ij} - v_j^-)^2}\, j = 1, 2, \dots, m} \quad (6)$$

- Calculation of the relative closeness to the ideal solution

$$\boldsymbol{C_i^* = \frac{S_i^-}{S_i^* + S_i^-}, \quad i = 1, 2, \dots, m \wedge 0 < C_i^* < 1} \quad (7)$$

- Arrangement of alternatives in order of the closest to ideal to furthest from ideal that is the creation of a ranking. The alternative with $\boldsymbol{C_i^*}$ closest to 1 is the best preference among the possible options.

Searching for alternatives.

The dataset concerns different organic syntheses procedures for benzoic acid (BA) and γ-valerolactone (GVL). Only syntheses procedures showing significant differences among themselves and fully characterized (no missing datapoints) published in recent years are selected. Moreover for BA three more classical synthesis procedures are included – Cannizzaro reaction, oxidation of alkylbenzenes and carboxylation of phenylmetallics. The latter one is developed within green chemistry framework.

Assessment criteria

Parameters such as reactants, atom economy, efficiency, time and reactions conditions (temperature, pressure), solvents, catalysts and additional reagents are involved in evaluation as assessment criteria. Their descriptions are gathered in Table 1.

Table 1. Criteria involved in organic synthesis evaluations

Parameter	Unit	Description
Reactants	point	Starting material that acts as a substrate in an synthesis (mostly contributes the greatest number of carbon atoms to the product).
Atom Economy	%	The metrics that measures the efficiency of a synthetic process, in terms of the mass substrate atoms incorporated into the product molecule (ratio between the mass of desired product to the total mass of reactants).

Efficiency	%	The ratio of moles of product to moles of reactant (called yield or reaction yield).
Temperature	°C	The reaction conditions that are needed for obtaining product according to synthesis protocol.
Pressure	MPa	The reaction conditions that are needed for obtaining product according to synthesis protocol.
Time	h	The estimated total time required to manufacture the product according to synthesis protocol.
Solvent	point	The substance in which the reaction takes place.
Catalyst	point	The substance that increases reaction rate.
Reagent	point	Other substances that are needed for obtaining product according to synthesis protocol.

The majority of input data for analysis are taken from source scientific papers and patents. Some information concerning chemical hazards are provided by the Material Safety Data Sheets (MSDS) mainly from Sigma Aldrich and Merck companies webpages.

The selection of criteria is dictated by fulfilling the need to comprehensively refer to green chemistry principles. The second aspect is that criteria datapoints should be easily available, unequivocal, in numerical form or easily calculable into the numbers. Therefore, some descriptive information are transformed into numerical data. Due to fact that application of different reactants, catalysts, solvents and chemical reagents may influence environmental, health and safety impacts of the synthesis, the risks of chemical substances are expressed by pictograms. For this purpose, pictograms and codes compliant with The Global Harmonized System (GHS) related to physical, health and environmental hazards (or their combinations) are used[24,25]. Accordingly, each of them are described by number of points, in a range 0-10. The points are summed up if more than one pictograms label given chemical. The descriptions of the pictograms with assessed points are presented in Table S1 of Supplementary Information.

Unfortunately, some characteristics of chemicals are not fully available, mainly in case of catalysts, therefore due to lack of data, chemicals are substituted with the values of the chemically similar compounds/group of compounds as proposed by Adler et al.[26]. Suggested substituents are summarized in Table S2. In reference to precautionary principle, in case of available several datapoints, always the most unbeneficial one is selected.

Starting materials, solvents, catalysts and other reactants are defined using above described approach. In case of temperature and pressure, it is assumed that the optimum are room temperature (20°C) and atmospheric pressure (0.1 MPa). Therefore, the datapionts for these criteria are calculated as absolute values between a given process temperature/pressure and the optimal conditions. The numerical values for all criteria are summarized in Tables S3 and S4 (datasets prepared for MCDA analysis).

One of the most important part of MCDA procedure is assigning weights to criteria to give them relative importance in accordance to the purpose of the evaluation. Appropriate weights are assigned to the individual criteria to adjust to practical applications of the organic syntheses. The criteria weights are obtained on the basis of surveys obtained from two experts.

Results and Discussion

Two examples of assessments are given – the first one is intended to be scholar reaction – synthesis of benzoic acid (BA) from different substrates but mainly from benzene. The second synthesis is recently of great interest – obtaining of γ-valerolactone (GVL) mainly from levulinic acid. GVL is obtained from cellulosic biomass and it is considered to be platform chemical[27]. It is the substrate to obtain fuels and greener solvents[28] or polymers[29].

Weights for criteria

Table 2 presents the weights assigned by two experts to datasets of procedures for BA and GVL synthesis. Experts gave weights to criteria with 0 – 10 points scale according to their perception of the criteria importance. Then the points were normalized so their sum is equal to 1 and were introduced into TOPSIS algorithm.

The weights for first three criteria are similar for BA and GVL syntheses. In both cases it is unnecessary to work with gaseous substances, in case of BA the reactants are benzene and CO or CO_2, in case of GVL they are levulinic acid and H_2 or O_2. From the environmental point of view it can be assumed that application of carbon oxides is less advantageous than the application of oxygen or hydrogen. Efficiency and atom economy are important criteria but in both cases they are not discriminators, similarly to temperature and pressure. The reaction time is similar in case of BA dataset, while in case of GVL the values are significantly different – from 30 seconds to 13 hours, so the assigned weights are different. The similar situation is in case of 'solvent' parameter. Procedures for GVL are characterized by diversity from solventless (procedure 11), through water based or IL based (procedure 7) to procedure 8 that applies chlorobenzene. BA syntheses are always performed in solvents but solvents of different polarity. The 'catalyst' criterion is differentiating for BA procedures dataset while in case of GVL all procedures require the application of catalyst.

Expert 2 assigned different weights to the criteria for both datasets, with following justification. Reactants applied in some BA synthesis procedures are characterized with high risks (benzene and CO) while the most reactants used for GVL synthesis are benign and bio-based. Atom Economy and Efficiency are important criteria as they are both related to amounts of generated wastes. Atom Economy is given the weight equal to 5 in case of BA because of small variability of this criterion values. Temperature, pressure and time are criteria of lesser importance is terms of procedures greenness. The most of procedures for GVL synthesis apply water or alcohols as solvents so the weight is lower than in case of BA, where more diversed situation is observed. Catalyst is given low score in case of GVL as all procedures apply catalysts,

higher score is given to catalyst criterion in case of BA dataset. Only one procedure requires the application of reagent in GVL dataset, significantly different reagents are applied.

Table 2. Weights applied for rankings of BA and GVL synthesis procedures assigned by two experts.

Criterion	BA		GVL	
	Expert 1	Expert 2	Expert 1	Expert 2
Reactant	8	8	8	3
Atom Economy	6	5	8	10
Efficiency	8	8	8	8
Temperature	4	5	4	3
Pressure	4	4	4	4
Time	1	3	7	3
Solvent	7	7	8	5
Catalyst	8	5	5	3
Reagent	6	8	5	2

Benzoic acid synthesis procedures ranking.

The main paragraph text follows directly on here. The description of the dataset together with references to the source papers are presented in Table S3. The result of TOPSIS algorithm application is presented in Table 3. Despite application of slightly different weights the rankings results are very similar and can be discussed together. The order of top four procedures in both rankings is the same. Procedures 16, 17 and 18 start with other reactants than highly hazardous benzene, do not require catalyst, apply nonhazardous solvents, such as water or cyclopentyl methyl ether (assessed with solvent selection guide as having some known issues[26]). Particularly interesting from its greenness point of view is procedure 18, which applies a fluidized bed reactor under continuous flow conditions. Procedure 4 is based on benzene as the reactant but it applies no additional solvent, benign catalyst ($AlCl_3$) and reagent. It is characterized by mild temperature conditions (30°C) and relatively short synthesis time of 12.5 hours. While searching for green synthesis of benzoic acid it is recommended to pay special attention to these four procedures.

The procedures that are ranked at the lowest positions are 6, 5, 3, 14 and especially 13 with considerably lower similarity to ideal solution scores than last-but-one procedure (0.38 vs 0.438 according to expert 1 ranking and 0.358 vs 0.498 according to expert 2 ranking). Procedure 13 applies benzene and carbon monoxide as reactants, the reaction efficiency is only 36%. 1,1,1,3,3,3-hexafluoro-2-propanol and methanol are used as solvents, problematic catalysts and reagents are applied. The remaining procedures ranked at positions 5 – 13 are within quite narrow ranges of similarity to ideal solutions values of 0.655 – 0.744 for ranking according to expert 1 weights and 0.597 – 0.727 for ranking according to expert 2 weights. This is an implication that they are not significantly different in term of their greenness.

Table 3. Rankings of procedures for BA synthesis according to weights assigned by two experts

Rank	Expert 1		Expert 2	
	Procedure	Similarity to ideal solution	Procedure	Similarity to ideal solution
1	16	0.895	16	0.88
2	4	0.83	4	0.819
3	17	0.806	17	0.78
4	18	0.792	18	0.739
5	7	0.744	10	0.727
6	2	0.741	7	0.715
7	10	0.738	2	0.714
8	9	0.709	9	0.667
9	15	0.685	15	0.662
10	12	0.684	12	0.657
11	1	0.681	1	0.651
12	11	0.667	11	0.634
13	8	0.655	8	0.597
14	6	0.636	5	0.577
15	5	0.619	3	0.562
16	3	0.566	6	0.543
17	14	0.438	14	0.498
18	13	0.38	13	0.358

GVL synthesis procedures ranking

The description of the procedures for GVL synthesis and their references are presented in Table S4. The final rankings of procedures according to the weights assigned by two experts are presented in Table 4. It should be noted that experts assigned weights in more significantly differing way than it is in case of benzoic acid synthesis procedures rankings. In both cases the winning procedure is 11, with no solvent applied, green catalyst and reactant with moderate time (6 h), efficiency (65%) and Atom Economy (73.5%). In the remaining parts of rankings some shifts are present due to differences in the weights. For instance, the ranks for procedures 12 and 10 are 10 and 11 respectively, for expert 1 ranking, while for the same procedures the ranks are 13 and 8 with expert 2 weights ranking. The only procedure that applies reagent, procedure number 4 is ranked at last, 13th position according to expert's 1 weights and 12th position according to expert's 2 weights. What is interesting, procedures 12 and 13 are recommended by their authors as green are ranked 8th and 10th by Expert 1 weights ranking and 7th and 13th with Expert 2 weights. It is mainly because of application of problematic compounds as catalysts. Despite certain differences, both rankings are generally similar.

Table 4. Rankings of procedures for GVL synthesis according to weights assigned by two experts

Rank	Expert 1		Expert 2	
	Procedure	Similarity to ideal solution	Procedure	Similarity to ideal solution
1	11	0.803	11	0.775
2	2	0.727	7	0.759
3	7	0.715	8	0.699
4	3	0.701	2	0.678
5	9	0.699	3	0.623
6	8	0.694	9	0.618
7	6	0.676	13	0.602
8	13	0.629	10	0.600
9	5	0.578	6	0.595
10	12	0.574	5	0.593
11	10	0.573	1	0.592
12	1	0.548	4	0.559
13	4	0.467	12	0.526

Advantages and limitations of MCDA ranking approach.

The advantage of MCDA approach in comparison to atom economy is that many other factors are considered, such as energy consumption, toxicity and other hazards related to usage of reactants, solvents, catalysts and auxiliary substances. In fact atom economy, as presented above, can be easily incorporated into MCDA as one of criteria. The correlations between atom economy and similarities to ideal solutions for respective rankings are low. The determination factors are 0.13 and 0.14 for expert 1 and expert 2 in case of BA synthesis procedures rankings, respectively (with negative correlation). For GVL synthesis the determination factors are also very low 0.02 and 0.18 for expert 1 and 2, respectively. These lacks of correlations are strong implications that for more comprehensive greenness assessment, atom economy is not enough. Metric systems applying many criteria that refer to other aspects of greenness are required.

On the other hand, MCDA is much simpler than life-cycle assessment (LCA) approach. LCA is very detailed assessment approach, what is not always needed. It combines impacts from different categories and presents it as single score i.e. equivalent to kg of CO_2 emitted. MCDA also combines different criteria into single score (similarity to ideal solution in case of TOPSIS) but the advantage is that raw data is used for comparison between synthesis procedures. Recalculation of criteria values to impact scores such as kg of CO_2 emitted is always the potential source of error or bias. LCA is considered to be time-consuming assessment approach and requires to be performed by well-trained assessor.

Another advantage of MCDA is flexible analysis by selection of assessment criteria and giving them different relative importance. In the presented examples we propose the set of criteria that comprehensively describe the greenness of synthesis and are characterized by the ease of calculation or extraction of datapoints. However, the user may wish to include also other criteria. They may be the reactants availability or bio-based origin (principle 7 of green chemistry), easiness of on-line process monitoring (principle 11 of green chemistry). Fit-for-purpose assessment is the great advantage of MCDA.

Another feature of MCDA application is comparative approach, so the results refer only to synthesis procedures under consideration. Including another procedure in the assessment brings the need to run the algorithm again. The results of assessments by different rankings in form of similarities to ideal solutions are also not comparable. The advantage of MCDA application as comparative metrics system is the ease of finding differences between alternatives. On the other hand, the disadvantage is the lack of information on the weak points of synthesis procedures. To find the aspects that could be improved it is needed to move back to the dataset and investigate the values of the raw datapoints.

In comparison to other scoring metrics based on 12 principles presentation with spider diagram, MCDA has an advantage of more systematic way to combine criteria into final score and obtain ranking. It can also deal with more alternatives as in case of 4 or more of them spider diagram results are hard to interpret or impossible to read. In this context, the disadvantage of MCDA is lack of information on performance according to different criteria, so finding points to be improved requires coming back to raw dataset.

Conclusions

In this study we present easy way to make the comparative assessment of synthesis procedures greenness. We show that assessment system, being more comprehensive than single score metrics and much more simple than LCA, is highly needed. We show applicability on the two different examples of synthesis, benzoic acid that is quite scholar synthesis and γ-valerolactone that is recently the synthesis of great interest. We propose the set of criteria that cover the requirements of green chemistry assessment, being simple to calculate or extract from the literature sources.

The presented approach can be easily applied to select the greenest procedure from few or many procedures available. Another application is the assessment of newly developed synthesis procedure greenness in relation to previously developed synthesis procedures for the same purpose

Conflicts of interest

There are no conflicts to declare.

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