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Sustainability metrics for eco-technologies assessment, part I: preliminary screening

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Abstract This work presents a preliminary screening of eco-technologies for dimethyl carbonate (DMC) production. Through sustainability metrics, the assessment of six different chemical routes allows comparisons according to economical and environmental criteria, to determine the most sustainable route. CO_2 sequestration potential is also considered. The alternatives are scored according to the adopted metrics, leading to the decision of a suitable route based on economic and environmental grounds, prioritizing pollution-preventing technologies herein referred to as eco-technologies. Casting of technologies was based on alternatives available in the literature: *Route 1* production of DMC from methanol and phosgene [Ono in Pure Appl Chem 68(2):367–375, 1996]; *Route 2* production of DMC from methyl nitrite and CO [Ono in Pure Appl Chem 68(2):367–375, 1996]; *Route 3* production of DMC from CO and methanol [Ono in Pure Appl Chem 68(2):367–375, 1996]; *Route 4* production of DMC from urea and methanol (Wang et al. in Ind Eng Chem Res 46:8972–8979, 2007); *Route 5* production of DMC from ethylene oxide and CO_2 [Ono in Pure Appl Chem 68(2):367–375, 1996]; *Route 6* production of DMC from CO_2 and methanol (Choi et al. in Green Chem 4:230–234, 2002). The analysis shows that Routes 4 and 5 combine intermediate values of the total (sustainability) score, CO_2 sequestration potential and industrial feasibility, therefore entitled as eco-technologies, based on the adopted metrics. Although the two technologies are potentially ecological, they are recommended for a more rigorous analysis on the grounds of process simulation and life cycle analysis.

Keywords Sustainability assessment · CO_2 sequestration · DMC production · LCA

List of symbols

PP_j	Profit potential of Route *j*
PP_{best}	Best result obtained for routes profit potential
PI_j	Profit index of Route *j*
v_{ji}	Stoichiometric coefficient of Chemical *i* on Route *j*
P_{ji}	Price in US$/mol of Chemical *i* on Route *j*
TX_j	Toxicity of Route *j*
TX_{best}	Best result obtained for routes' toxicity
tx_{ji}	Toxicity of Chemical *i* on Route *j*
TXI_j	Toxicity index of Route *j*
EI_j	Environmental impact of Route *j*
EI_{best}	Best result obtained for routes' environmental impact
$Score_{Total,j}$	Total score or Route *j*

Introduction

Environmental performance of products and processes has gained importance as the industry is trying to minimize its effects over environment, using management tools such as life cycle analysis (LCA) (Krotscheck and Narodoslawsky, 1996). Climate effects due to the rise of CO_2 concentration in atmosphere are among the main concerns of society targets. Thus, there is a search for processes that use this

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greenhouse gas as a raw material, defined as chemical sequestration.

Dimethyl carbonate (DMC) market is broadening, so that DMC is moving to the category of chemical commodity: it can be used, for example, as alkylation agent, gas or diesel additive and as a monomer in polycarbonate synthesis (Xiaolu et al. 2006; Aresta et al. 2001). The expanding market can therefore accommodate a production expansion represented by higher CO_2 sequestration target.

In the present work, the production of DMC from different chemical routes is evaluated to establish, at a preliminary screening, whether production is sustainable. The sustainability metric takes into consideration both economical and environmental aspects. In this context, the status "eco-technology" is granted to profitable (and therefore feasible) technologies that cause minimal environmental distress.

This study consists of a preliminary screening of six routes for DMC production (three of which have CO_2 sequestration potential), briefly described as follows:

- Route 1: production of DMC and coproduction of HCl from methanol and phosgene (Ono 1996)
- Route 2: production of methyl nitrite from methanol and NO, followed by production of DMC from methyl nitrite and CO, recovering NO (Ono 1996)
- Route 3: production of DMC and water from CO and methanol (Ono 1996)
- Route 4: production of DMC and NH_3 from urea and methanol (urea production involves CO_2 sequestration) (Wang et al. 2007)
- Route 5: production of DMC and ethylene glycol from ethylene oxide and CO_2 (Ono 1996)
- Route 6: production of DMC and water from CO_2 and methanol (Choi et al. 2002).

It is important to notice that Routes 4–6 show CO_2 sequestration potential. Figure 1 is a scheme of the six chemical routes.

Aresta and Galatola (1999) present a LCA for comparison between Routes 1 and 4. The authors report that Route 1 is around four times more impacting than Route 4. The other routes are cited, but do not take part in LCA.

In this study, relevancy was placed on the need, at early stage of process development, of simple metrics for decision support, for screening process alternatives. By applying simpler metrics, it is possible to compare a larger range of routes obtaining easily understandable results.

Methodology

The choice for one DMC production route among the six presented alternatives must comply with a sustainability criterion that allows for ranking process candidates according to the adopted score. Anatas and Allen (2002) present a very simple method for ranking different routes economically. Fan et al. (2007) presents an equally simple method for ranking different routes environmentally.

Furthermore, the waste reduction algorithm (WAR) is a more detailed algorithm that has a metric for quantifying the environmental impact (EI) of a process. This method

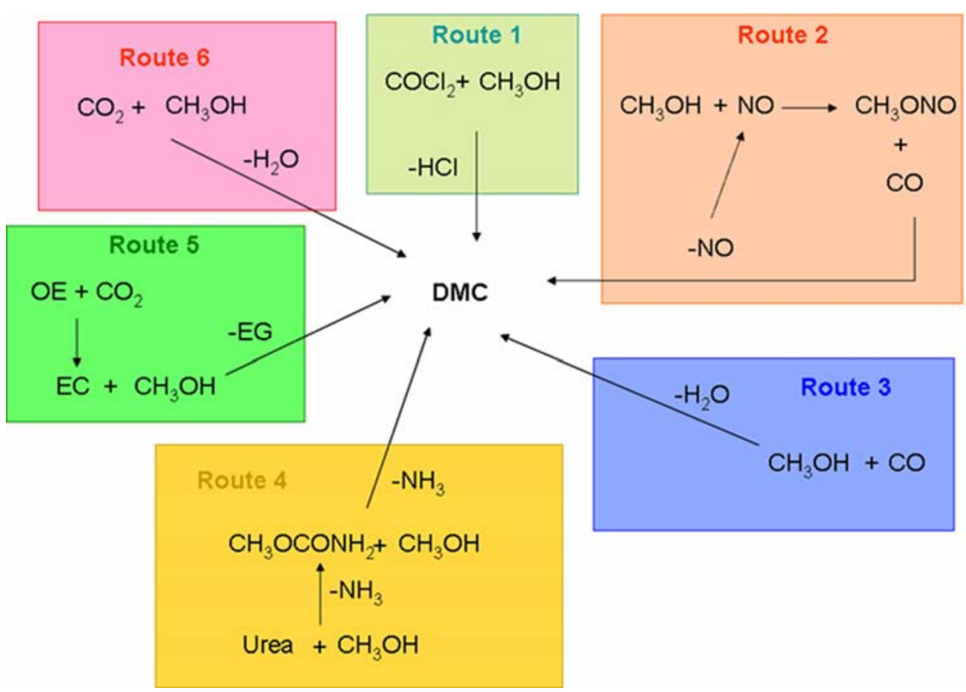

Fig. 1 Routes for DMC production

was also applied to the six routes. WAR complexity is equivalent to Aresta and Galatola's (1999) adopted procedure.

The preliminary screening herein presented consists of applying these two methods to the following: (1) selecting the most promising routes among a selected set of alternatives; (2) evaluating the performance of Fan et al.'s (2007) environmental ranking method against WAR application.

The first step of the preliminary screening consists of organizing a table of stoichiometric coefficients of the chemicals used in each of the six routes. Intermediate chemicals must appear in this table, even though their stoichiometric coefficients are zero, so that they are considered in toxicology and EI analysis. Also, since these analyses must consider the product's life cycle (here divided into cradle-to-gate and gate-to-gate domains), raw chemicals were included in the table. It means for instance that, once methanol is used in DMC production, synthesis gas (raw material for methanol production) will figure in the table.

To build the economical ranking, the profit potential (PP) of each route must be estimated. It is considered that the processes under analysis happen in ideal conditions, with total conversion of reactants into products. Given this, the PP can be calculated as the difference between products and reactants prices, weighted by stoichiometric coefficients. The routes that do not show PP in this preliminary criterion must be eliminated (Fan et al. 2007).

As discussed, for the environmental ranking, this study works with a dual approach based in hazards assessment: (1) a toxicity ranking, as proposed by Fan et al. (2007), and (2) an EI ranking, using WAR, as a modification of the method proposed by Aresta and Galatola (1999). The toxicity index is calculated based on NFPA's health risk factor for each chemical, while the WAR algorithm calculates indexes that represent the EI (measured in PEI/h) of a process (Hossain et al. 2007; Jensen et al. 2003). The impact categories used for calculation of EI are as follows:

1. HTPI: human toxicity potential by ingestion
2. HTPE: human toxicity potential by exposure
3. TTP: terrestrial toxicity potential
4. ATP: aquatic toxicity potential
5. GWP: global warming potential
6. ODP: ozone depletion potential
7. PCOP: photochemical oxidation potential
8. AP: acidification potential

In this study, the software WAR GUI (available on the internet at http://www.epa.gov) was used for applying the WAR algorithm. The software has a databank of chemicals with physical, chemical and safety properties. To compare the route's performance as a whole, the results of the economical, toxicity and EI analyses are combined to generate a total score.

Results

Table 1 shows the stoichiometric coefficients for the chemicals used in each of the six DMC production routes. If the coefficient is zero, it means that the chemical is an intermediate. Multiplication sign (×) was used in the cradle-to-gate domain to indicate the presence of the chemical in the route. Table 2 shows the chemical's prices, in US$/mol (only for chemicals involved in gate-to-gate domain).

Table 1 DMC production routes

Chemical	Route 1	Route 2	Route 3	Route 4	Route 5	Route 6
Stoichiometric coefficients (gate-to-gate domain)						
Hydrochloric acid	2					
Water		1	1			1
Ammonium				1		
Ethylene carbonate					0	
Dimethyl carbonate	1	1	1	1	1	1
Carbon dioxide					−1	−1
Ethylene glycol					1	
Phosgene	−1					
Methanol	−2	−2	−2	−3	−2	−2
Methyl carbamate				0		
Carbon monoxide		−1	−1			
Methyl nitrite		0				
Ethylene oxide					−1	
Nitric oxide		1				
Oxygen		−1/2	−1/2			
Urea				−1		
Cradle-to-gate domain						
Carbon	×	×	×	×	×	×
Sodium chloride	×					
Chlorine	×					
Carbon dioxide				×		
Ethane					×	
Ethylene					×	
Hydrogen	×	×	×	×	×	×
Methane	×	×	×	×	×	×
Carbon monoxide	×	×	×	×	×	×
Nitrogen				×		
Oxygen		×	×		×	

Table 2 Chemical's prices

Chemical	Price (US$/mol)	Source
Hydrochloric acid	0.00342	Icis Pricing
Ammonium	0.00496	Icis Pricing
Carbon credits	0.00084	Chicago Climate Exchange
Dimethyl carbonate	0.10810	Indian Chemicals
Ethylene Glycol	0.06238	Icis Pricing
Phosgene	0.16571	Innovation Group
Methanol	0.01047	Icis Pricing
Carbon monoxide	0.00140	Praxair, Linde Gas
Ethylene oxide	0.05487	Icis Pricing
Nitric oxide	0.00150	Praxair, Linde Gas
Oxygen	0.00477	Praxair
Urea	0.02019	Icis Pricing

Profit potential and profit index (PI) were calculated according to Eqs. 1 and 2. For the sake of comparison, Route 4 was taken as basis (PI = 1).

$$\mathrm{PP}_j = \sum_{i=1}^{n} v_{ji} P_{ji} \quad (1)$$

$$\mathrm{PI}_j = \frac{\mathrm{PL}_j}{\mathrm{PL}_4} \quad (2)$$

where $\mathrm{PP}_j = \mathrm{PP}$ of Route j; $\mathrm{PI}_j = \mathrm{PI}$ of Route j; v_{ji} = stoichiometric coefficient of Chemical i on Route j; P_{ji} = price in US$/mol of Chemical i on Route j. The result is shown in Fig. 2. Route 1 is the only nonprofitable among the six analyzed routes. Route 5 has the highest PP, followed by Routes 6, 2, 3 and 4, respectively.

To create the toxicity ranking, the health risk indexes for the chemicals involved were added, resulting in the routes' toxicity (Eq. 3). Then, the toxicity index of each route was calculated, using Route 4 as reference basis (Eq. 4).

Fig. 2 Economical ranking of alternative routes

$$\mathrm{TX}_j = \sum_{i=1}^{n} \mathrm{tx}_{ji} \quad (3)$$

$$\mathrm{TXI}_j = \frac{\mathrm{TX}_j}{\mathrm{TX}_4} \quad (4)$$

where TX_j = toxicity of Route j; tx_{ji} = toxicity of Chemical i on Route j; TXI_j = toxicity index of Route j.

Finally, for the WAR algorithm, it was considered that the processes receive 1 kg/h of each reactant (pure component) and give a product flow of 1 kg/h. This data is fed to WAR GUI software, which responds each route EI.

Although it is possible to set different weights for each impact category, we opted to set all weights to unity, since giving each criterion the same importance is the simplest way of addressing this problem. Note that this preliminary screening must be as simple as possible and gives a quick but still precise answer. It is clear that adding weights (according to each case study needs) can help giving a more precise answer. The results for both approaches are shown in Figs. 3 and 4.

It is worth noting that the toxicity index results are in general agreement with the EI results (given by WAR). Route 1, which earned the last position on economical

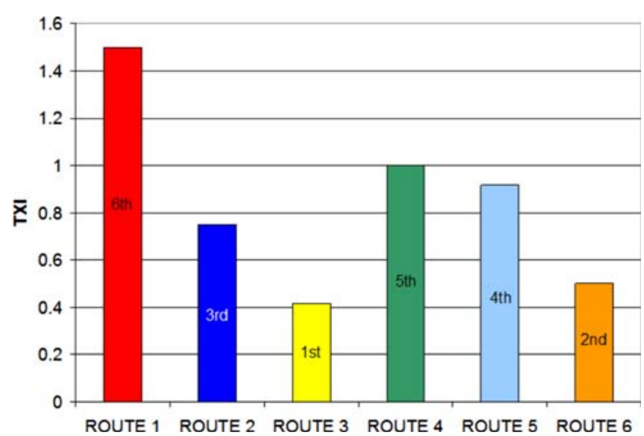

Fig. 3 Toxicity ranking of alternative routes

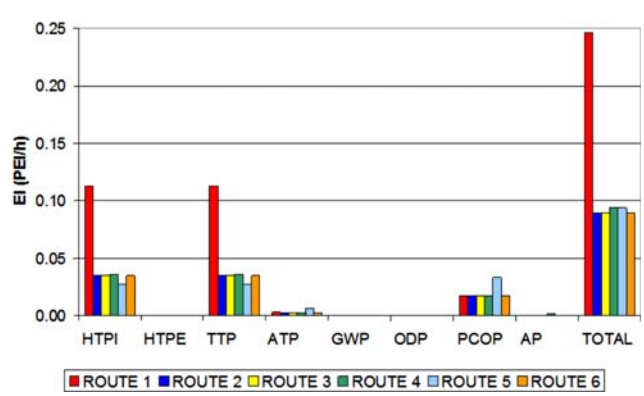

Fig. 4 Environmental impact ranking based on WAR algorithm

ranking, had also the worst performance in environmental ranking (on both EI and toxicity criteria). According to the toxicological approach, Routes 2, 4 and 5 show intermediate environmental performance, while Routes 3 and 6 are considered "greener." WAR positions Routes 4 and 5 as intermediates and Routes 2, 3 and 6 as "greener."

Table 3 summarizes routes' performance in each category and as a whole. The results of the economical, toxicity and EI analyses are combined to generate a total score, according to Eq. 5:

$$\mathrm{Score}_{\mathrm{Total},j} = \left(\frac{\mathrm{TX}_j - \mathrm{TX}_{\min}}{\mathrm{TX}_{\max} - \mathrm{TX}_{\min}}\right) + \left(\frac{\mathrm{EI}_j - \mathrm{EI}_{\min}}{\mathrm{EI}_{\max} - \mathrm{EI}_{\min}}\right) + \left(\frac{\mathrm{PP}_{\max} - \mathrm{PP}_j}{\mathrm{PP}_{\max} - \mathrm{PP}_{\min}}\right) \quad (5)$$

The total score of each route represents the sum of the relative distances between the route's TX, EI and PP functions and the best values found. Then, the lower the total score, the greener the route. Note that, in the cases of EI and TX functions, the best value is the lower bound, while for PP function, it is the upper bound. The results are given in Table 3.

In accordance with the results obtained by Aresta and Galatola (1999), Route 1 is almost four times more impacting than Route 4. Fan et al.'s (2007) environmental ranking method's results, using toxicity as environmental index, were qualitatively equal to the results generated by WAR application. The quantitative normalized results, however, were different. This can be observed by comparing TX and EI columns.

Another relevant issue is that the EIs of the routes (except for Route 1) are very close. This means that, in this study case, EI plays almost no role in discerning between the routes.

Equation 5 (relative distance) is only one of the many ways of aggregating the functions in question. Alternatively, we could have decided for Eq. 6, which presents Euclidian distance. This option, however, requires that the functions be multiplied by factors to guaranty the same order of magnitude (otherwise, the parcels with low order of magnitude would be of no importance in the sum).

Table 3 Routes' total score

Route	$\frac{TX_j - TX_{min}}{TX_{max} - TX_{min}}$	$\frac{EI_j - EI_{min}}{EI_{max} - EI_{min}}$	$\frac{PP_{max} - PP_j}{PP_{max} - PP_{min}}$	Total score
1	1.00	1.00	1.00	3.00
2	0.31	0.00	0.06	0.37
3	0.00	0.00	0.07	0.07
4	0.54	0.03	0.20	0.77
5	0.46	0.03	0.00	0.49
6	0.08	0.00	0.04	0.12

$$\mathrm{Score}_{\mathrm{Total},j} = \sqrt{0.01\left(\mathrm{TX}_j - \mathrm{TX}_{\mathrm{best}}\right)^2 + \left(\mathrm{EI}_j - \mathrm{EI}_{\mathrm{best}}\right)^2 + \left(\mathrm{PP}_j - \mathrm{PP}_{\mathrm{best}}\right)^2} \quad (6)$$

In this study case, function TX requires a scaling factor of 1/100. Using this factor, Eqs. 5 and 6 lead to the same ranking for the routes. Again, it is possible to set different weights for each function (TX, EI and PP) in both Eqs. 5 and 6. Similarly as done before, we opted to set all weights to unity (except, of course, for the scaling factor) to keep the method simple.

Conclusions

Six chemical routes for DMC synthesis were compared by means of their economical and environmental performances, with the objective of reducing the number of routes to be compared in a more detailed analysis (for example, LCA) to find the most sustainable route.

The preliminary screening shows that Route 1—production of DMC from phosgene—has the worst results (both economically and environmentally). This route, then, must not be used for DMC production. The screening also indicates that Routes 3 and 6 are the greener routes. Route 5, on the other hand, has a better PP and its total score seems to be a bearable result (fourth place).

If CO_2 sequestration is used as an additional selection criterion, both Routes 2 and 3 must be abandoned, and although Route 6's results are very good, this route must be eliminated because there is no indication that it is feasible in industrial scale. Table 4 summarizes route's total score and limitations. Based on these global results, Routes 4 and 5 should be considered eco-technologies, since they combine intermediate total score, sequestration potential and industrial feasibility.

The method used herein, however simple, were capable of detecting two eco-technologies among the six technologies assessed, but given the simplicity of the methods, the two eco-technologies detected should be evaluated on the ground of process simulation and LCA, before taking any conscious decision.

Table 4 Routes' final performance

Route	Total score	Final ranking	Limitation
1	3.00	Sixth	None
2	0.37	Third	No CO_2 sequestration
3	0.07	First	No CO_2 sequestration
4	0.77	Fifth	None
5	0.49	Fourth	None
6	0.12	Second	Not feasible industrially

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