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# Sustainability metrics for eco-technologies assessment, Part II. Life cycle analysis

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**Abstract** This work presents a sustainability analysis of $CO_2$ reuse to produce dimethyl carbonate (DMC) via ethylene oxide (ROUTE A) and via urea methanolysis (ROUTE B). Two different technologies are considered in ROUTE A: reaction followed by separation and reactive distillation. Life cycle analyses of the ROUTES are presented employing sustainability analysis performed in HYSYS process simulator, along with WAR Algorithm. Process economical optimization is performed to maximize the processes profitability. A sustainability function, defined as a 2D indicator involving both economical and environmental aspects, is calculated for the optimized processes. Additional sustainability indexes are evaluated: material index, energy index, and ecoefficiency. The results, under both economical and environmental aspects, show that ROUTE A is the most sustainable. The study also points to the relevance of the frontier set between the domains cradle-to-gate and gate-to-gate in assessing process sustainability during LCA.

**Keywords** Sustainability metrics · $CO_2$ sequestration · LCA

## List of symbols

| | |
|---|---|
| $K$ | Arrhenius pre-exp. factor |
| $E_A$ | Activation energy |
| $N$ | Column's number of trays |
| $x_{i,\mathrm{top}}$ | Molar fraction of component $i$ in distillate |
| $x_{i,\mathrm{bot}}$ | Molar fraction of component $i$ in bottoms |
| $\mathrm{rec}_{i,\mathrm{top}}$ | Molar fraction of component $i$ recovered in distillate |
| $\mathrm{rec}_{i,\mathrm{bot}}$ | Molar fraction of component $i$ recovered in bottoms |
| $V$ | Volume ($m^3$) |
| $\mathrm{SF}_i$ | Sustainability function of route i |
| $P_i$ | Profit of route (US$/year) |
| $T_i$ | Temperature of stream $i$ (°C) |
| $\mathrm{EI}_i$ | Environmental impact of route $i$ (PEI/y) |
| $\mathrm{EI}_{m,i}$ | Modified environmental impact of route $i$ (PEI/y) |
| $\omega_P$ | Weight of function $P$ (year/US$) |
| $\omega_{\mathrm{EI}}$ | Weight of function EI (year/PEI) |
| $\omega_k$ | Weighting factor associated to function $k$ |
| $M_{\mathrm{CO2},i}$ | Mass of $CO_2$-eq emitted in route $i$ (kg) |
| $M_{\mathrm{product},i}$ | Mass product obtained in route $i$ (kg) |
| $C$ | Equipment cost (US$) |
| $F_c$ | Correction factor |
| $H$ | Equipment height (ft) |
| $D$ | Equipment diameter (ft) |
| M&S | Marshall and Swift index |
| $A$ | Heat transfer area ($ft^2$) |
| $LD_{50}$ | Median lethal dose |
| $M$ | Material index |
| $E$ | Energy index (kJ/kg) |
| $\varepsilon$ | Ecoefficiency |
| $p$ | Products mass flow (kg/h) |
| rm | Raw materials mass flow (kg/h) |
| $e$ | Energy consumption (kJ/h) |
| ec | Economical indicator |
| en | Environmental indicator |

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## Introduction

Monteiro et al. (2008) present a procedure for screening eco-technologies approaching six possible routes for dimethyl carbonate (DMC) production. The study aimed to assess sustainability and pointed towards routes of production from ethylene oxide (ROUTE A) and urea (ROUTE B), considered by the authors as the most promising alternatives for chemical reuse of $CO_2$ (chemical sequestration), contributing to the mitigation of global warming effects.

In the present work, a life cycle analysis (LCA) is conducted for ROUTES A and B in order to deepen the sustainability assessment. The processes were conceived in two domains: cradle-to-gate and gate-to-gate (Hossain et al. 2007). Gate-to-grave domain is excluded from LCA as DMC is taken for promising fuel substitute (or additive) to diesel or gasoline. As any organic fuel, DMC use will ultimately lead to $CO_2$ emissions. However, its use is considered benefic since, according to Wang et al. (2000), each 10% DMC addition to diesel leads to 20% smoke reduction. This and other uses for DMC would yield a market volume of 30 Mt/year (Zevenhoven et al. 2006).

As gate-to-gate domain is the actual industrial venture in focus, processes of cradle-to-gate domain are herein seen as auxiliary, and were addressed exclusively to allow LCA. In this sense, there are other possible processes for producing the required raw materials that are not considered but could equally have been used.

For the gate-to-gate domain analysis, DMC production processes are simulated and optimized using HYSYS (Hyprotech Inc.). The environmental impact (EI) of each route is assessed using the WAR methodology (Cabezas et al. 1999), which relates the potential EI to measurable quantities, such as $LD_{50}$. For this purpose, the WAR algorithm as presented by Young et al. (2000) is implemented in HYSYS. Differently, the cradle-to-gate domain is analyzed using technical data of greenhouse gas emissions available from Cetesb (2009)—a Brazilian Environmental Agency, Werder and Steinfeld (2000) and the Environmental Protection Authority of Australia (2002).

**Table 1** ROUTE A: kinetic constants of Reactions I and II

| Reaction | *K* | $E_A$ (J $mol^{-1}$) |
|---|---|---|
| I | 109 (mol $L^{-1}$ $s^{-1}$) | 37200 |
| II: Forward | 10.98 ($mol^{0.2}$ $L^{-0.2}$ $s^{-1}$) | 37200 |
| II: Reverse | 198 (mol $L^{-1}$ $s^{-1}$) | 57000 |

Source: Cui et al. (2004)

Both routes are conceived to produce 150 kgmole/h of DMC, which corresponds to approximate DMC production of 97.28 t/year. The analysis herein presented sets the frontier between the domains as to include the chemical reuse of $CO_2$ inside gates, as presented in the sequence.

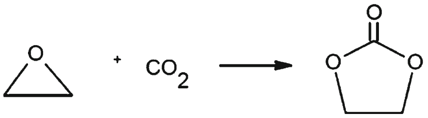
## Process conception for ROUTES A and B

### ROUTE A: DMC from EO

### *Gate-to-gate domain*

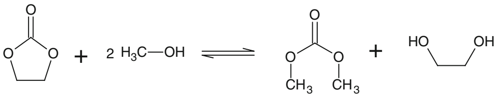
Reactions involved in the domain gate-to-gate are

(1) Ethylene carbonate (EC) formation



(reaction I)

(2) DMC and ethylene glycol (EG) formation.



(reaction II)

Notice that ethylene oxide (EO) production process generates a purge stream with $CO_2$ (mole fraction of approx. 0.12). ROUTE A explores the synergy between EO and DMC production processes, since EO itself is used as a sequestration agent (Reaction I). Cui et al. (2004) report the kinetics for Reaction II and consider Reaction I as instantaneous. In this work, it is assumed that Reaction I is ten times faster than Reaction II, and has the same activation energy, as shown in Table 1.

The equilibrium of Reaction II limits EC conversion to a range from 50 to 80%, as estimated by Fang and Xiao (2004). The authors have therefore opted to carry out this step *n* in a reactive distillation column, thereby shifting the equilibrium towards DMC, which enables 100% EC conversion. However, Fang and Xiao (2004) conducted the reaction in a batch distillation column filled with 1,400 ml of methanol but fed with EC at the rate of 0.5 ml/min, which results in a MeOH:EC ratio unpractical for industrial processes.

According to Thotla and Mahajani (2009), integration of reaction with separation in a single unit offers distinct advantages over conventional sequential approach, reaction followed by separation. Therefore, the present work investigates two continuous process configurations for DMC production from OE:

ROUTE A 1: OE and $CO_2$ are fed into a *P*, where Reaction I takes place; the EC produced reacts with methanol (Reaction II) in a second PFR, producing DMC and EG;

ROUTE A 2: EC, produced in a PFR as in ROUTE A1, is fed along with methanol into a reactive distillation column with middle vessel configuration (Bezzo and Barolo 2005).

*Flowsheets description* In both configurations A1 and A2, Reaction I takes place in PFR-100 (Figs. 1, 2), where EO conversion reaches 100%, at 180°C and 60 bar. As $CO_2$ is added to the reactor in excess, it has to be recovered from the outlet flow. Under reaction conditions, the gas is highly miscible with EC, and therefore is mostly in the liquid phase. However, when pressure is dropped to 1 atm and temperature is lowered to 50°C, 97.8% of the gas can be recovered and then recycled. The liquids pass through a water absorber, so that EC can be recovered with 100% purity. The remaining $CO_2$ is liberated in a purge stream.

In configuration A1, the EC produced and methanol are fed into PFR-101, where EC conversion to DMC reaches 64%. The reactor operates at 50 bar and 180°C. The outlet stream has its pressure dropped to 1 atm and is sent to a separation unit consisting of three distillation columns. In column T-100, DMC is 99.7% recovered in the distillate (with the methanol) while E.G is 100% recovered in the bottoms (with the EC). Columns T-101 and T-103 purifies the products up to 99% molar. The unreacted raw material is recycled to PFR-101.

In configuration A2, EC and methanol are fed into the MVC. Column configuration was investigated by successive simulations in order to establish the number of trays in the rectifier section and the stripper section so that the distillate is free of E.G and the bottom stream has no DMC. In the final arrangement, the rectifier (T-100) has 14 trays and the stripper (T-102) has five trays. Distillate composition is 82.5% methanol, 17.5% DMC. Bottoms composition is 75.4% EC, 24.6% E.G. Both distillate and bottom products are sent to distillation columns (T-10X and T-10Y), for DMC and EG purification up to 99%. The unreacted raw material is recycled to reaction vessel V-100.

As both methanol content in the stripper and EC content in the rectifier are low, and since the catalyst (a strong alkali, such as KOH) would not be present in the rectifier, the reaction is restricted to the vessel. The simulations were conducted using UNIQUAC thermodynamic model. Flowsheet equipment is described in more details in Tables 2 and 3.

## Cradle-to-gate domain

Cradle-to-gate domain consists of the following associated processes:

1. Ethylene production from ethane (obtained from natural gas—NG—and oil);
2. EO production from ethylene and oxygen;
3. Syngas production by steam methane reform; and
4. Methanol production from syngas.

According to Cetesb (2009), emission factors for ethylene and EO production processes are, respectively, 0.95 $tCO_2$-eq/t ethylene, and 0.86 $tCO_2$-eq/t EO. Werder and Steinfeld (2000) report total emissions for the conventional syngas production as 1.04 $tCO_2$-eq/t syngas (molar ratio $H_2$:CO = 2:1). Finally, the Environmental Protection Authority of Australia (2002) reports an emission factor of

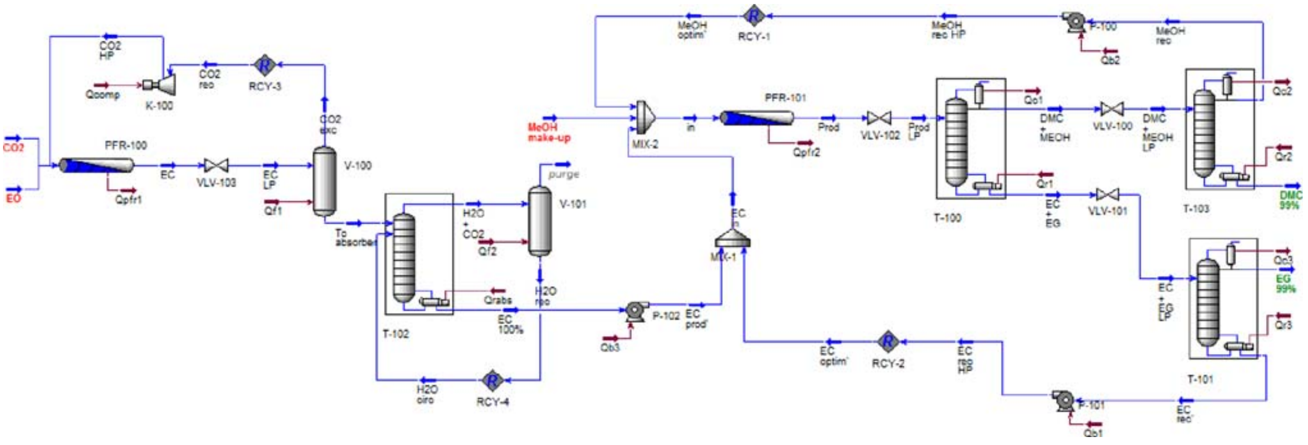


Fig. 1 ROUTE A1: gate-to-gate domain process flowsheet

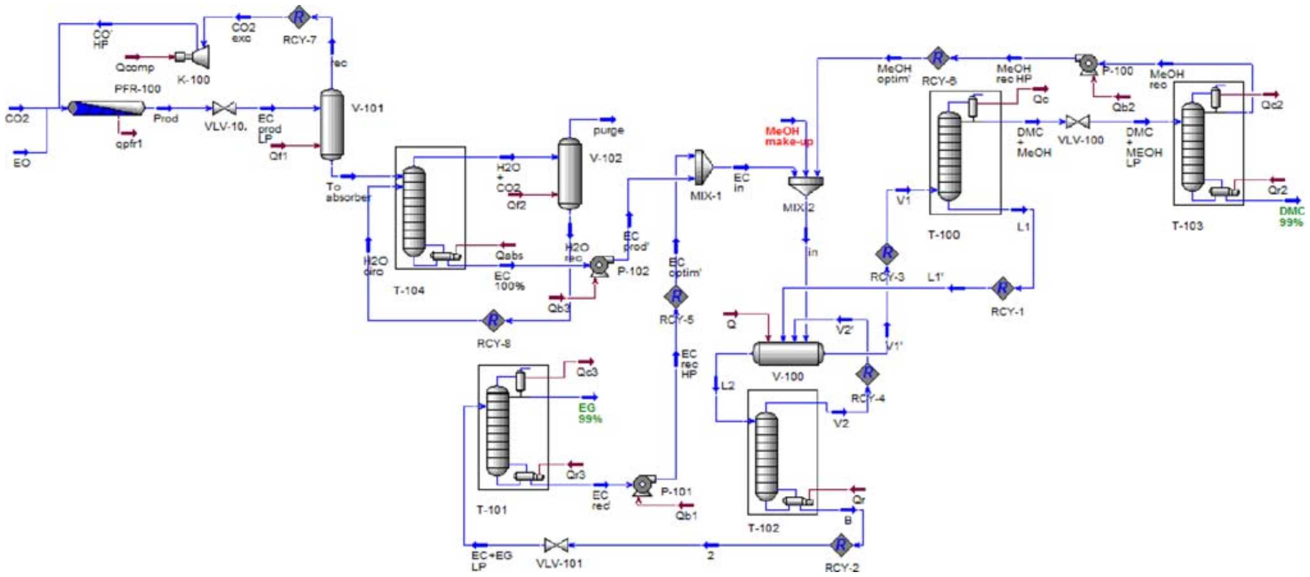


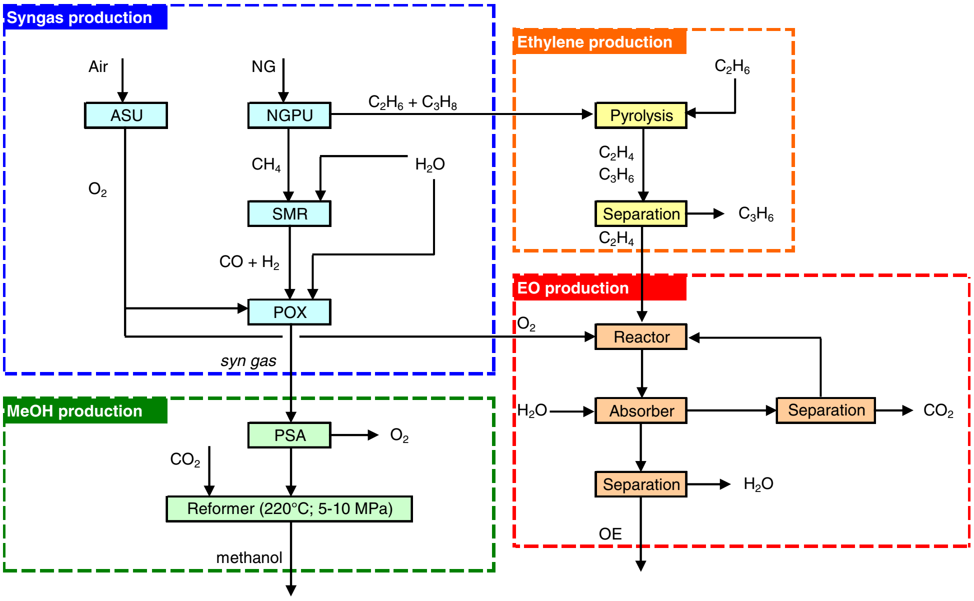
**Fig. 2** ROUTE A2: gate-to-gate domain process flowsheet

**Table 2** ROUTE A1: flowsheet equipment

| Tag | Equipment | Specifications |
|---|---|---|
| PFR-101 | Plug flow reactor | $V = 15$ m$^3$, $L = 7$ m, $T = 180$°C |
| PFR-100 | Plug flow reactor | $V = 75$ m$^3$, $L = 11.6$ m, $T = 180$°C |
| T-101 | Distillation | $N = 25$, $x_{\mathrm{EG,top}} = 0.99$, $\mathrm{rec}_{\mathrm{EG,top}} = 0.998$ |
| T-103 | Distillation | $N = 15$, $x_{\mathrm{DMC,top}} = 0.99$, $\mathrm{rec}_{\mathrm{DMC,top}} = 0.998$ |
| T-100 | Distillation | $N = 25$, $\mathrm{rec}_{\mathrm{DMC,top}} = 0.997$, $\mathrm{rec}_{\mathrm{EG,bot}} = 1$ |
| P-100 | Pump | Duty = 41.7 hp |
| P-101 | Pump | Duty = 27.5 hp |
| P-102 | Pump | Duty = 49.7 hp |
| V-100 | Separator | $T = 50$°C |
| V-101 | Separator | $T = 25$°C |
| K-100 | Compressor | Duty = 601 hp |
| T-102 | Reboiled absorber | $\mathrm{rec}_{\mathrm{EC,bot}} = 0.98$ |

**Table 3** ROUTE A2: flowsheet equipment

| Tag | Equipment | Specifications |
|---|---|---|
| T-100 | Refluxed absorber | $x_{\mathrm{EG,top}} = 3.5\mathrm{e} - 7$ |
| T-102 | Reboiled absorber | $x_{\mathrm{DMC,bot}} = 1\mathrm{e} - 4$ |
| T-104 | Reboiled absorber | $\mathrm{rec}_{\mathrm{EC,bot}} = 0.98$ |
| V-100 | Separator | $V = 70$ m$^3$, $T = 180$°C |
| V-101 | Separator | $T = 50$°C |
| V-102 | Separator | $T = 25$°C |
| T-101 | Distillation | $N = 25$, $x_{\mathrm{EG,top}} = 0.99$, $\mathrm{rec}_{\mathrm{EG,top}} = 0.998$ |
| T-103 | Distillation | $N = 15$, $x_{\mathrm{DMC,top}} = 0.99$, $\mathrm{rec}_{\mathrm{DMC,top}} = 0.998$ |
| P-100 | Pump | Duty = 10.5 hp |
| P-101 | Pump | Duty = 21.7 hp |
| P-102 | Pump | Duty = 9.1 hp |
| PFR-100 | Plug flow reactor | $V = 15$ m$^3$, $L = 7$ m, $T = 180$°C |
| K-100 | Compressor | Duty = 601 hp |



| | |
|---|---|
| ASU | Air Separation Unit |
| NGPU | NG Processing Unit |
| SMR | Steam Methane Reformer |
| POX | Partial Oxidation Unit |
| PSA | Pressure Swing Adsorption |

**Fig. 3** ROUTE A: cradle-to-gate domain process flowsheet

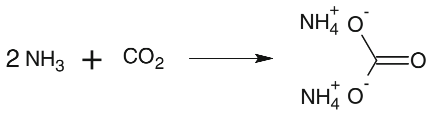
0.412 $tCO_2$-eq/t methanol produced. The integrated process is represented in the flowsheet of Fig. 3.

ROUTE B: DMC from urea

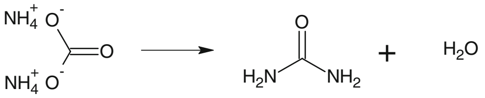
*Gate-to-gate domain*

Gate-to-gate domain consists of urea production from ammonia and $CO_2$, followed by DMC production by urea methanolysis, involving the following steps:

(1) urea production;

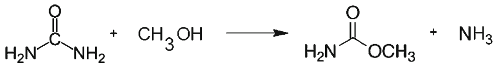


(Reaction III)



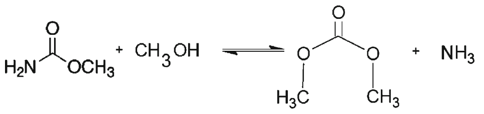
(Reaction IV)

(2) methyl carbamate (MC) production;



(Reaction V)

(3) DMC production.



(Reaction VI)

Although urea production process was not object of simulation in this study, its ISBL and utility costs were evaluated so that the process sustainability could be assessed (in "Sustainability function"). It is relevant to note that the ammonium necessary for urea production can be obtained from Reactions V and VI, if the unreacted raw material is completely recycled and considering no process losses. Global process reaction shows that $CO_2$ and methanol are the only raw materials needed in gate-to-gate

**Table 4** ROUTE B: kinetic constants for reactions V and VI

| Reaction | $K$ ($\text{mol}^{-1}$ L $\text{s}^{-1}$) | $E_A$ (J $\text{mol}^{-1}$) |
|---|---|---|
| V | $1.10 \times 10^3$ | $1.10 \times 10^5$ |
| VI | $1.464 \times 10^{-3}$ | $4.90 \times 10^4$ |

Source: Wang et al. 2007

domain of ROUTE 4. Similarly, the only products generated are DMC and water.

The flowsheet simulated in HYSYS contemplates MC and DMC productions, plus a vapor generation unit capable of supplying the utility vapor demanded in urea production unit. Reaction VI, as presented by Wang et al. (2007), is conducted in a reactive distillation column, using heterogeneous catalyst (ZnO). Adopted kinetic constants of Reactions V and VI are shown in Table 4.

*Flowsheet description* Gate-to-gate domain processes are simulated in HYSYS using UNIQUAC thermodynamic package (see Fig. 4). Urea is diluted in methanol and then fed to a vessel (V-100), where Reaction V takes place, reaching 100% urea conversion. MC and methanol are sent to a reactive distillation column with 42 trays, and divided into three sections: absorption (from trays 1 to 18); reaction (from trays 19 to 26); and stripping (from trays 27 to 42). The reaction temperature is controlled by setting temperature in the 22nd tray in 189°C. Figure 5 shows temperature profile along the column and Fig. 6 presents composition profile of the liquid phase.

The gas flows into a distillation column (T-102) where methanol is recovered and ammonium is purified up to 99.8%. The bottom stream of reactive distillation contains DMC, the unreacted MC and residual methanol. This stream is fed into column T-100, where MC is recovered. The stream containing methanol and DMC flows to T-101, which recovers methanol and produces DMC with 99.5% purity. Purified DMC pre-heats the methanol stream fed into reactive column. The equipment is detailed in Table 5.

### Cradle-to-gate domain

The cradle-to-gate domain consists of syngas and methanol production processes. Both processes figure in ROUTE A cradle-to-gate domain and were already discussed in this work.

## Sustainability function

### Function definition

Sustainability is understood as the balance of the three dimensions of sustainable development: economic, environmental, and societal (Martins et al. 2007). In chemical process evaluation, however, it is usually calculated as a two-dimensional indicator, considering both economical and environmental aspects. This work presents a 2D indicator for sustainability assessment of ROUTES A and B;

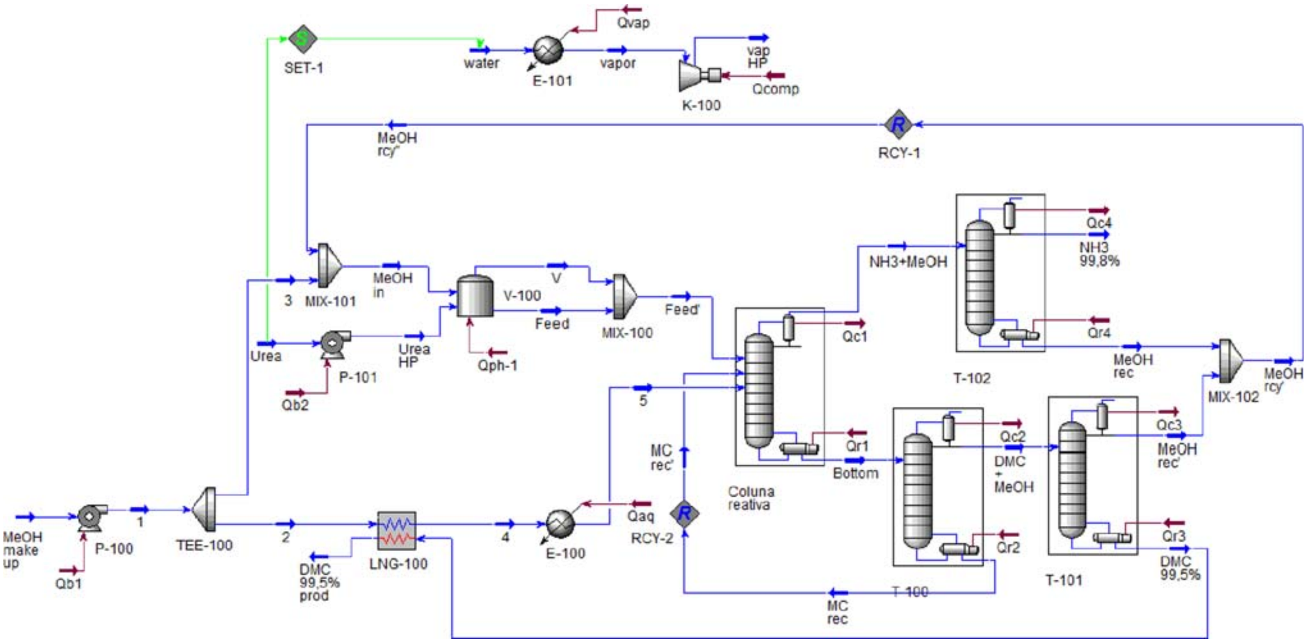


**Fig. 4** ROUTE B: gate-to-gate domain process flowsheet

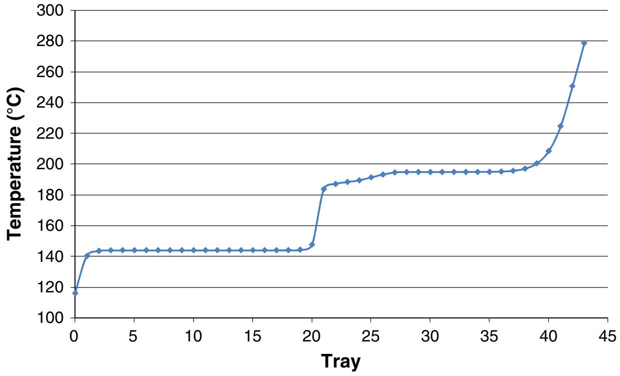


**Fig. 5** ROUTE B: temperature profile along the reactive column

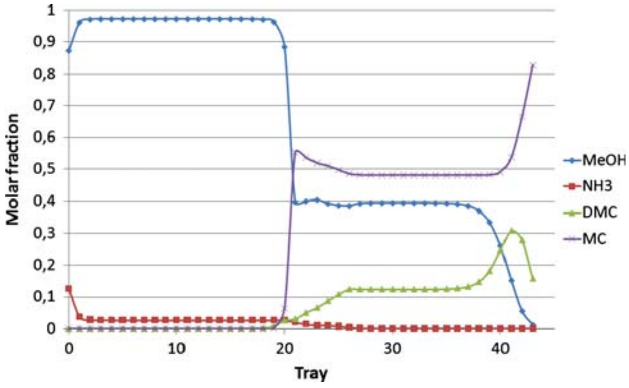


**Fig. 6** ROUTE B: liquid phase composition profile along the reactive column

the herein proposed sustainability function (SF) is shown in Eq. 1a, 1b:

$$\mathrm{SF}_i = \omega_P P_i - \omega_{\mathrm{EI}} \mathrm{EI}_{m,i} \tag{1a}$$

$$\mathrm{EI}_{m,i} = \mathrm{EI}_i \frac{M_{\mathrm{CO}_2,i}}{M_{\mathrm{product},i}} \tag{1b}$$

where $\mathrm{SF}_i$ = sustainability function of route $i$, $P_i$ = profit of route $i$, $\mathrm{EI}_{m,i}$ = modified environmental impact of route $i$, $\omega_k$ = weighting factor associated to function $k$, $\mathrm{EI}_i$ = environmental impact of route $i$; $\mathrm{M}_{\mathrm{CO2},i}$ = mass of $\mathrm{CO}_2$-equivalent emitted in route $i$, $\mathrm{M}_{\mathrm{product},i}$ = mass of product obtained in route $i$.

Choosing the best eco-technology is a multi-objective problem. The multi-criteria optimization in focus is a vector of decision variables (process variables) which satisfies constraints (operational, economical and environmental) and optimizes a vector of functions whose positions represents objective functions ($P$ and EI).

The ratio $\omega_P/\omega_{\mathrm{EI}}$ is the relevant measure. As it tends to zero, the choice of a technology will rely exclusively on environmental issues. On the other hand, as $\omega_P/\omega_{\mathrm{EI}}$ tends to infinity, classical profitability function will guide the selection. The weighting factors are tuning factors on controlling sustainability aspects. In fact, if no trade-off exists, i.e., if economic and environmental indexes are affected by design variables in the same direction, $\omega_P$ and $\omega_{\mathrm{EI}}$ are irrelevant.

The weighting factors can be tuned so that one of the two considered aspects (economical and environmental) is given more relative importance than the other. Note that, as *SF* is proposed as a difference, if $P_i$ and the $\mathrm{EI}_{i,m}$ have different orders of magnitude, it can become insensitive to one of these two aspects. Therefore, to avoid dominancy of one aspect over another, the weighting factors must be set to compensate for eventual differences in magnitude.

## Environmental impact (EI) function

The waste reduction algorithm (WAR), which characterizes sustainability with an index that measures potential environmental impacts (PEI), is selected to calculate EI of DMC production in each route (Young et al. 2000). EI is measured in "PEI" per unit of time. Although the algorithm defines eight hazard categories, only four of them are considered: human toxicity potential by ingestion (HTPI), human toxicity potential by inhalation or dermal exposure (HTPE),

**Table 5** ROUTE B: flowsheet equipment

| Tag | Equipment | Specifications |
|---|---|---|
| | Reactive distillation column | $N = 42$, $T = 189$°C (tray#22), $x_{\mathrm{MeOH,bot}} = 0.01$ |
| T-100 | Distillation | $N = 16$, $x_{\mathrm{MC,bot}} = 0.999$, $x_{\mathrm{MeOH,bot}} = 1\mathrm{e}-4$ |
| T-101 | Distillation | $N = 10$, $x_{\mathrm{DMC,bot}} = 0.99$, $\mathrm{rec}_{\mathrm{DMC,bot}} = 0.997$ |
| T-102 | Distillation | $N = 10$, $x_{\mathrm{NH3,top}} = 0.998$, $x_{\mathrm{NH3,bot}} = 1\mathrm{e}-7$ |
| V-100 | Tank | $V = 12.95\ \mathrm{m}^3$, $T = 80$°C |
| P-100 | Pump | Duty = 8.5 hp |
| P-101 | Pump | Duty = 4.7 hp |
| LNG-100 | LNG | $\mathrm{T}_{\mathrm{hot,out}} = 60$°C |
| E-100 | Heater | $T_{\mathrm{vapor}} = 100$°C |
| E-101 | Heater | $T_5 = 180$°C |
| K-100 | Compressor | Duty = 7,200 hp |

aquatic toxicity potential (ATP), and global warming potential (GWP). The four remaining categories are omitted based on the following considerations: (a) terrestrial toxicity potential, TTP, is actually proportional to HTPI since both are measured using chemicals $LD_{50}$; (b) according to data provided by Anastas and Allen (2002), none of the chemicals involved in ROUTES A and B present ozone depletion potential (ODP) or acidification potential (AP); and (c) the only chemical that has Photochemical Oxidation Potential (PCOP) in both routes is methanol, so that this category can be directly evaluated comparing flow rates. And, since ROUTES A and B use the same amount of methanol, PCOP of both routes are the same.

For $EI_m$ evaluation, it is necessary to calculate greenhouse gas (GHG) releases associated with each process, reported as $CO_2$-equivalent. In this work, the emissions due to operation are calculated as a function of the energy demand of the equipment used in each plant. The facilities are considered to employ natural gas as fuel. Transportation emissions and gas losses due to process inefficiencies are considered negligible.

### Profit ($P$) function

The annual profit ($P$) of each process is calculated according to Eq. 2 (Knapp and Doherty 1990). The revenue and the costs of raw material and utilities are calculated in USD/year, while the ISBL is given in USD. Utilities' cost correlations are displayed in Table 6 and Douglas' (1988) correlations for ISBL are summarized in Table 7.

$$P = \text{Revenue} - \text{ISBL} - (\text{raw material} + \text{utilities}) \qquad (2)$$

Additional considerations are that the plants operate for 7,200 h/year; $CO_2$ is assumed available at no cost, and its consumption is actually part of the revenue, since it generates carbon credits (each ton of $CO_2$ pays USD 19.02); the Marshal and Swift index (M&S) is set in 1,274.8, referring to the year 2005; ISBL for urea production plant was estimated from the values reported by van Baal and Lemmen (2003).

### Process optimization

Prior to SF calculation, the process configurations i and ii (ROUTES A1 and A2) are optimized for maximal profit.

**Table 6** Cost of utilities

| Cost of utilities | |
|---|---|
| Vapor | USD 6.98/t |
| Water | USD 6.90e-3/$m^3$ |
| Electrical energy | USD 0.43/kW h |

**Table 7** Cost of equipments correlations

| | Cost of equipments |
|---|---|
| Heat exchangers | $C = \frac{\text{M\&S}}{208} 101.3A^{0.65}(2.29 + F_c)$<br>$F_c = 0.85$<br>$A$ = heat transfer area ($ft^2$) |
| Vessels, columns and reactors | $C = \frac{\text{M\&S}}{208} 101.9D^{1.066}H^{0.802}(2.18 + F_c)$<br>$F_c = 1$<br>$D$ = diameter (ft)<br>$H$ = height (ft) |
| Internals of distillation columns | $C = \frac{\text{M\&S}}{208} 4.7D^{1.55}H \times F_c$<br>$F_c = 1$<br>$D$ = diameter (ft)<br>$H$ = height (ft) |
| Pumps | 30,000.000[a] |

Source: Douglas (1988)

[a] Estimated cost

### *ROUTE A1*

The decision variable (MeOH:EC feed ratio to PFR-101) impacts reactor volume and EC conversion per pass, as displayed in Fig. 7. Figure 8 shows profit dependence on the reactor volume. The optimal reactor volume is found to be 75 $m^3$, corresponding to MeOH:EC feed ratio to PFR-101 around 3.

### *ROUTE A2*

MeOH:EC feed ratio to V-100, the decision variable, affects both reactor volume and EC conversion per pass, as shown in Fig. 9. Figure 10 points to an optimal reactor volume of 70 $m^3$ (MeOH:EC feed ratio is around 1.5).

### *ROUTE B*

The chosen decision variable was MeOH:MC ratio fed into the reactive column. As the optimizer does not access

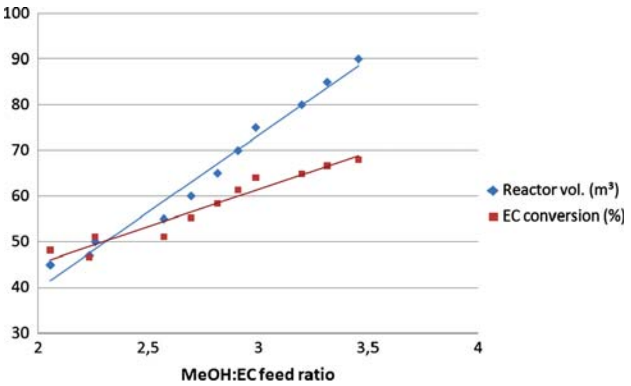


**Fig. 7** ROUTE A1: impact of MeOH:EC feed ratio on reactor volume and EC conversion per pass

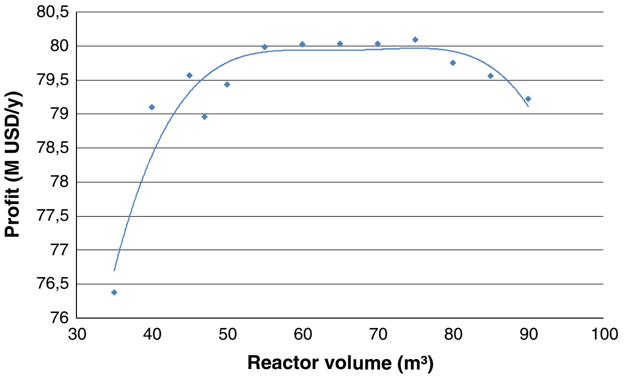


**Fig. 8** ROUTE A1: impact of reactor volume on profit

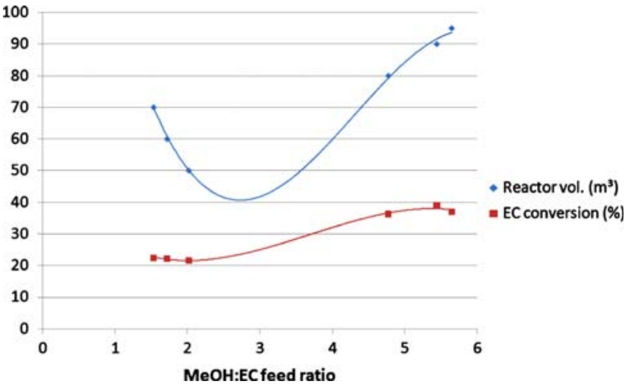


**Fig. 9** ROUTE A2: impact of MeOH:EC feed ratio on reactor volume and EC conversion per pass

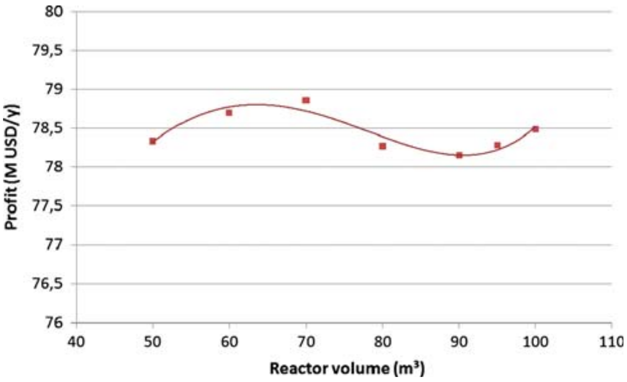


**Fig. 10** ROUTE A1: impact of reactor volume on profit

process configurations, the number of trays of the reacting section in the reactive column is fixed, which limits the reaction extent, leading to a short search range in MeOH:MC ratio. Figure 11 shows that conversion decreases with the increase of MeOH:MC feed ratio. Figure 12 shows that the optimal ratio is around 0.17.

Process material and energy streams of the three ROUTES in optimal operational condition are described in Tables 8 and 9.

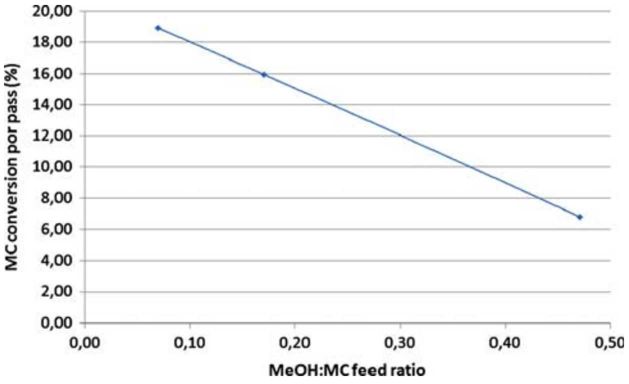


**Fig. 11** ROUTE B: impact of MeOH:MC feed ratio on MC conversion per pass

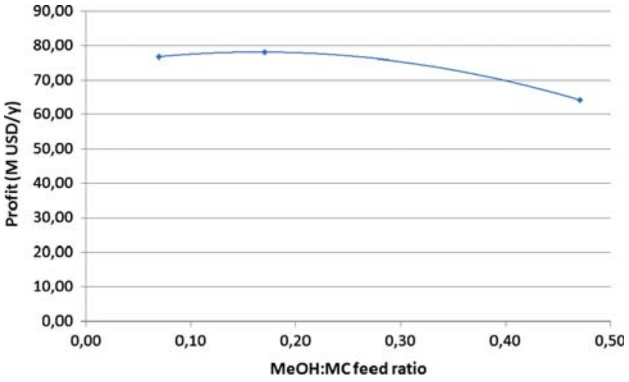


**Fig. 12** ROUTE B: impact of MeOH:MC feed ratio on profit

## SF results for gate-to-gate processes

The results of gate-to-gate analysis of ROUTES A1, A2 and B are shown in Table 10. The three options have similar profitability, ranging from 78.11 to 80.09 million USD/year. A relative basis is assumed for EI and SF functions, with $EI_{A1}$ and $SF_{A1}$ considered as unit. It can be seen that the two configurations of ROUTE A have very similar EI, which was already expected since they both share the same material balance. The difference between A1 and A2 is found in the energy use, a factor with clear-cut impact on $CO_2$-equivalent emissions.

On this ground, ROUTE A1 is undoubtedly the most sustainable evaluated technology: it not only presents the higher sequestration rate, but also the highest profit and the lowest environmental impact. These three aspects in assessing eco-technologies are captured into the highest relative SF. This conclusion, however, is constrained to gate-to-gate domain.

ROUTE A2 can be eliminated from the screening at this point since it is a worse option for gate-to-gate process than A1 and once both ROUTE A configurations necessarily have the same cradle-to-gate results.

**Table 8** Process main material streams

ROUTE A1

| | L1 | L2 | V1 | V2 | In | MeOH make-up | DMC 99% |
|---|---|---|---|---|---|---|---|
| Temperature | 176.92 | 180.00 | 180.00 | 251.73 | 147.36 | 64.50 | 89.69 |
| Pressure (kPa) | 800.00 | 800.00 | 800.00 | 800.00 | 800.00 | 800.00 | 101.32 |
| Mass flow (kg/h) | 3,141.50 | 145,326.08 | 39,233.82 | 95,537.89 | 85,907.65 | 9,618.73 | 13,529.38 |
| | EG 99% | EC rec HP | MeOH rec HP | $CO_2$ | EO | Purge | $H_2O$ rec |
| Temperature | 197.25 | 248.55 | 64.82 | 192.00 | 120.00 | 25.00 | 25.00 |
| Pressure (kPa) | 101.32 | 800.00 | 800.00 | 6,000.00 | 6,000.00 | 101.32 | 101.32 |
| Mass flow (kg/h) | 9,296.34 | 40,491.83 | 22,562.94 | 6,676.27 | 6,608.10 | 76.79 | 2,080.15 |

ROUTE A2

| | In | MeOH make-up | DMC 99% | EG 99% | EC rec HP | MeOH rec HP | Prod |
|---|---|---|---|---|---|---|---|
| Temperature | 127.17 | 64.50 | 89.69 | 196.64 | 251.98 | 66.84 | 180.00 |
| Pressure (kPa) | 5,000.00 | 5,000.00 | 101.32 | 101.32 | 5,000.00 | 5,000.00 | 5,000.00 |
| Mass flow (kg/h) | 42,880.05 | 9,625.15 | 13,450.12 | 9,382.63 | 7,310.96 | 12,736.50 | |
| | EO | $CO_2$ | EC | $CO_2$ exc | EC 100% | Purge | $H_2O$ rec |
| Temperature | 120.00 | 192.00 | 180.00 | 50.00 | 248.00 | 25.00 | 25.00 |
| Pressure (kPa) | 6,000.00 | 6,000.00 | 6,000.00 | 101.32 | 101.32 | 101.32 | 101.32 |
| Mass flow (kg/h) | 6,608.10 | 6,676.82 | 16,453.69 | 3,168.87 | 13,204.04 | 76.66 | 2,080.20 |

ROUTE B

| | Urea | Feed | NH3 + MeOH | Bottom | MC rec | DMC + MeOH | NH3 99.8% |
|---|---|---|---|---|---|---|---|
| Temperature | 25.00 | 80.00 | 115.97 | 278.67 | 305.46 | 209.21 | 38.76 |
| Pressure (kPa) | 101.32 | 1,500.00 | 1,500.00 | 1,500.00 | 1,500.00 | 1,500.00 | 1,500.00 |
| Mass flow (kg/h) | 9,008.39 | 17,323.13 | 9,893.84 | 73,167.69 | 59,279.37 | 13,888.32 | 5,121.99 |
| | MeOH in | MeOH make-up | DMC 99.5% prod | Uréia HP | Water | Vap HP | MeOH rec |
| Temperature | 108.27 | 25.00 | 60.00 | 25.90 | 25.00 | 980.31 | 153.11 |
| Pressure (kPa) | 1,500.00 | 101.32 | 1,500.00 | 1,500.00 | 101.32 | 10,800.00 | 1,500.00 |
| Mass flow (kg/h) | 8,314.86 | 9,612.57 | 13,526.03 | 9,008.39 | 10,017.32 | 10,017.32 | 4,771.86 |

## Life cycle assessment

The analysis is next expanded to include cradle-to-gate domain in a life cycle assessment. This evaluation was conducted taking into consideration the data for $CO_2$-eq emission related in item 2. From this data, and knowing the stoichometric need of MeOH, EO, ethylene and syngas, it is possible to estimate emissions of each route, as displayed in Table 11.

The relevancy of raw material production for net $CO_2$-eq emission of each ROUTE is massive. ROUTE B, which has intermediate $CO_2$ sequestration capacity in gate-to-gate domain, presents the lowest $CO_2$-eq life cycle emission for DMC production. However, it is important to note that the gate-to-gate domain processes were simulated in HYSYS, and had their energy streams optimally integrated. If the same approach was applied in cradle-to-gate domain, the energy integration between processes would certainly lower this domain's $CO_2$-eq emissions.

A combined cradle-to-gate/gate-to-gate sustainability function can be written as

$$\mathrm{SF}_i = \omega_P P_i - \omega_{\mathrm{gtg}} \mathrm{EI}_{m,i}^{\mathrm{gtg}} - \omega_{ctg} \mathrm{EI}_{m,i}^{\mathrm{ctg}} \quad (3)$$

where $\mathrm{EI}_{m,i}^{\mathrm{gtg}}$ = modified EI of gate-to-gate domain of route $i$, $\mathrm{EI}_{m,i}^{\mathrm{ctg}}$ = modified EI of cradle-to-gate domain of route $i$, $\omega_{\mathrm{gtg}}$ = weighting factor of function EI of gate-to-gate domain; $\omega_{\mathrm{ctg}}$ = weighting factor of function EI of cradle-to-gate domain.

The weighting factors follow the same rationale as in Eq. 1a. Hossain et al. (2007) states that the emissions of the target process generally have greater impact on occupational health and safety and local population health as well as local ecological health, which should be given extra emphasis. This means that gate-to-gate domain should have more relevance then cradle-to-gate domain when comparing different processes. In the proposed equation, the importance grade of functions can be set by tuning of the weighting factors. Table 12 relates the importance grade of

**Table 9** Process energy streams

| ROUTE A1 | Heat flow (GJ/h) | ROUTE A2 | Heat flow (GJ/h) | ROUTE B | Heat flow (GJ/h) |
|---|---|---|---|---|---|
| Cooling streams | | | | | |
| Qc1 | 51.95 | Qc | 29.83 | Qc1 | 30.42 |
| Qc2 | 56.53 | Qc2 | 97.49 | Qc2 | 59.94 |
| Qc3 | 12.42 | Qc3 | 84.84 | Qc3 | 4.78 |
| Qf1 | 3.28 | Qf1 | 3.28 | Qc4 | 36.09 |
| Qf2 | 4.97 | Qf2 | 4.97 | Heating streams | |
| Qpfr1 | 4.22 | Qpfr1 | 3.37 | Qr1 | 35.03 |
| Qpfr2 | 3.89 | Q | 50.15 | Qr2 | 60.86 |
| Heating streams | | | | Qr3 | 4.91 |
| Qb1 | 0.07 | Qr | 87.99 | Qr4 | 25.33 |
| Qb2 | 0.11 | Qr2 | 90.11 | Qb1 | 0.02 |
| Qb3 | 0.13 | Qr3 | 73.48 | Qb2 | 0.01 |
| Qr1 | 44.39 | Qabs | 10.28 | Qph-1 | 1.96 |
| Qr2 | 56.73 | Qb1 | 0.06 | Qaq | 4.95 |
| Qr3 | 12.75 | Qb2 | 0.03 | Qvap | 25.77 |
| Qrabs | 10.28 | Qb3 | 0.02 | Qcomp | 19.41 |
| Qcomp | 1.61 | Qcomp | 0.77 | | |

**Table 10** LCA results: gate-to-gate domain

| | A1 | A2 | B |
|---|---|---|---|
| Gate-to-gate domain | | | |
| Profit (M USD/year) | 80.09 | 78.21 | 78.11 |
| Relative EI | 1.00 | 1.02 | 2.46 |
| Net Energy use[a] (TJ/year) | 216.37 | 681.77 | 414.99 |
| $CO_2$-eq emission[b] (t/year) | 10,788.84 | 33,995.54 | 20,692.95 |
| $CO_2$ reacted (t/year) | 47,521.10 | 47,516.25 | 47,821.55 |
| Net $CO_2$ sequestrated (t/year) | 36,732.26 | 13,520.70 | 27,128.61 |
| Relative SF | 1.00 | 0.31 | −0.13 |

[a] Considering heat integration of energy streams with 79.16% recovery of net heat possessed (Bulasara et al. 2008)

[b] Natural gas: HV = 37.23 MJ/m$^3$, density = 0,8 kg/m$^3$, $CO_2$-eq emission = 49.864 *t*/TJ (Aubé 2001)

**Table 11** LCA results: net $CO_2$-eq emissions

| ROUTE | A1 | B |
|---|---|---|
| Cradle-to-gate domain | Estimated $CO_2$-eq emission (t/year) | |
| Ethene production | 35,040.00 | – |
| EO production | 35,840.00 | – |
| Methanol production | 28,551.80 | 28,551.80 |
| Syngas production | 38,919.90 | 38,919.90 |
| Gate-to-gate domain | $CO_2$ sequestration (t/year) | |
| | 36,732.26 | 27,128.61 |
| Life cycle | Net $CO_2$-eq emission (t/year) | |
| | 101,619.4 | 40,343.1 |

**Table 12** Importance grade of function *i*

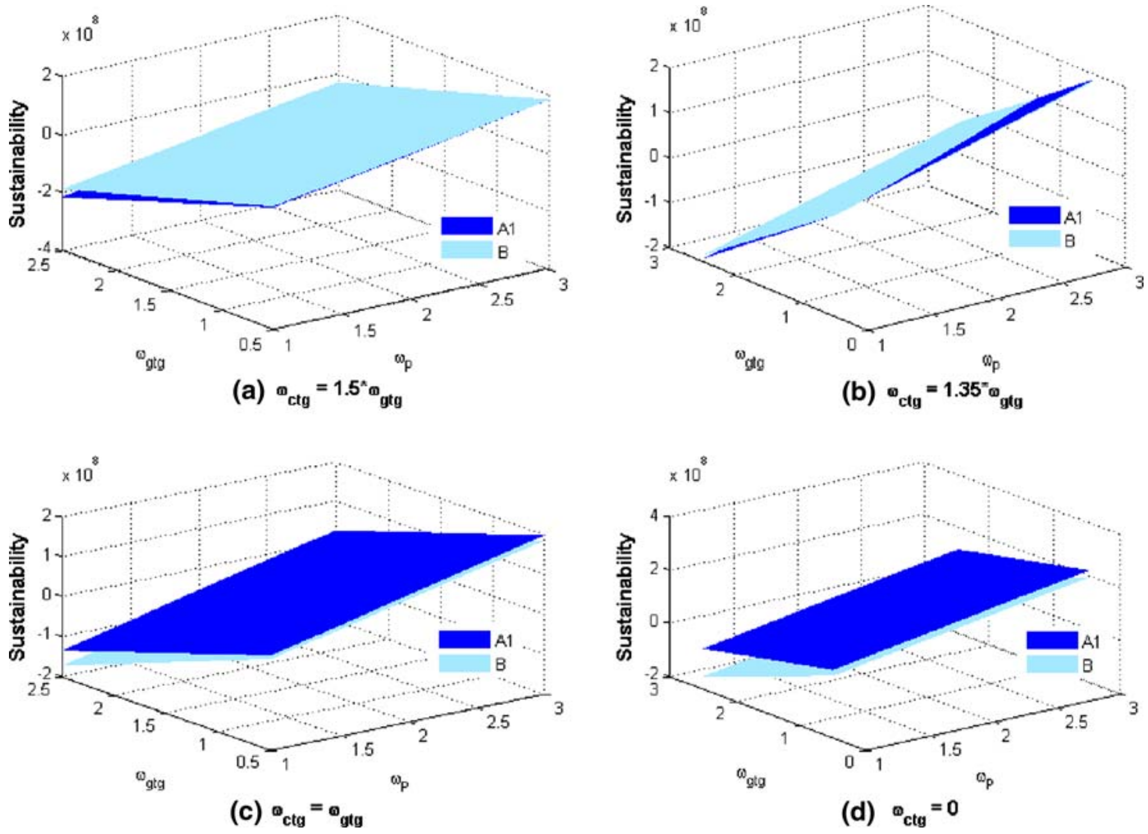
| Importance grade | | |
|---|---|---|
| Low | Normal | High |
| $0 \leq \omega_i < 0.75$ | $0.75 \leq \omega_i < 1.25$ | $\omega_i \geq 1.25$ |

**Table 13** LCA results: life cycle sustainability

| | A1 | B |
|---|---|---|
| Profit (M USD/year) | 80.09 | 78.11 |
| Relative $EI_{gtg}$ | 1.00 | 2.46 |
| Relative $EI_{ctg}$ | 1.00 | 0.45 |
| Relative SF | 1.00 | 0.52 |

the associated functions to their $\omega_i$ values. The LCA results for ROUTES A1 and B are displayed in Table 13 (considering $\omega_P = \omega_{gtg} = \omega_{ctg} = 1$).

Table 13 shows that ROUTE B has a better relative result for cradle-to-gate EI. And, as ROUTE A1 has lower EI in gate-to-gate domain, it is expected that the tuning of the weighting factors has an impact on route's relative sustainability. Figure 13 shows 3D graphs for the functions S00000F$_{A1}(\omega_P, \omega_{gtg})$ and $SF_B(\omega_P, \omega_{gtg})$. The four cases analyzed are (a) $\omega_{ctg} = 1.5\omega_{gtg}$; (b) $\omega_{ctg} = 1.35\omega_{gtg}$;(c) $\omega_{ctg} = \omega_{gtg}$, and (d) $\omega_{ctg} = 0$. In case (a), ROUTE B is the most sustainable one for any combination of weights in the studied range ($0.5 \leq \omega_{gtg} \leq 2.5$ and $1 \leq \omega_P \leq 3$). In case (b), the choice for the most sustainable ROUTE depends on which importance grade is given to both *P* and $EI^{gtg}$.



(a) $\omega_{ctg} = 1.5^{*}\omega_{gtg}$ (b) $\omega_{ctg} = 1.35^{*}\omega_{gtg}$

(c) $\omega_{ctg} = \omega_{gtg}$ (d) $\omega_{ctg} = 0$

**Fig. 13** Sustainability of ROUTES A and B. **a** $\omega_{ctg} = 1.5\omega_{gtg}$, **b** $\omega_{ctg} = 1.35\omega_{gtg}$, **c** $\omega_{ctg} = \omega_{gtg}$, and **d**.$\omega_{ctg} = 0$

Finally, in cases (c) and (d), ROUTE A1 is the most sustainable route.

Actually, cases (c) and (d) represent the frontier of a region that, according to Hossain et al. (2007), should be prioritized since the cradle-to-gate domain is considered less relevant than the gate-to-gate domain in any case between these two. Although cases (a) and (b) represent a relevance inversion, they were included in this study to illustrate the influence of weighting factors on the choice of an eco-technology.

The sustainability metric applied in the present work is one among many possibilities. To confirm relative SF results, sustainability is further analyzed according to three indexes presented by Marteel et al. (2003):

(1) Material index (*M*):

$$M = \frac{p}{\mathrm{rm}} \tag{4}$$

(2) Energy index (*E*):

$$E = \frac{e}{p} \tag{5}$$

(3) Ecoefficiency ($\varepsilon$):

$$\varepsilon = \frac{\mathrm{ec}}{\mathrm{en}} \tag{6}$$

where $p$ = products mass flow (kg/h), rm = raw material mass flow (kg/h), $e$ = energy consumption (kJ/h), ec = economical indicator, en = environmental indicator.

As economical index, Marteel et al. (2003) suggest the use of the value-added by the operation, and, as environmental index, the authors cite air quality. In this work, the environmental indicator adopted was the EI of gate-to-gate domain.

Applying these metrics to ROUTES A1 and B results in the values reported in Table 14. As ROUTE A1 generates only DMC and E.G from the raw material consumed, the material index is 1. ROUTE B, on the other hand, produces DMC and water. The produced water is consumed as utility, and this material “loss” is reflected on the material index. The energy index shows that ROUTE B consumes almost four times more energy than ROUTE A1 and, finally, ROUTE A1 is the most eco-efficient.

**Table 14** Sustainability metrics as proposed by Marteel et al. (2003)

| Metric | ROUTE A1 | ROUTE B |
|---|---|---|
| *M* (kg/kg) | 1.00 | 0.84 |
| *E* (MJ/kg) | 1.32 | 4.99 |
| ε (US\$/$PEI_{out}$) | 0.49 | 0.19 |

## Conclusions

This work approaches the production of DMC, described as a green fuel, to illustrate a methodology for sustainability assessment of eco-technologies, based on LCA. In a previous study, Monteiro et al. (2008) introduced a screening procedure for an early selection of potential process alternatives. The screening led to two alternatives employing $CO_2$ as raw material, an ecological approach for the production under consideration: ROUTES A and B, in which EO and ammonia, respectively, are used as co-reactants. The life cycle assessment of these ROUTES is performed through process simulation and optimization in HYSYS employing WAR algorithm for EI analysis.

In chemical process evaluation sustainability is usually calculated as a two-dimensional indicator, considering both economical and environmental aspects. Therefore, choosing the best eco-technology is a multi-objective problem. The multi-criteria optimization in focus is a vector of decision variables (process variables) which satisfies constraints (operational, economical and environmental) and optimizes a vector of functions whose positions represents objective functions (*P* and EI). To address this problem, this work proposes a scalar objective function, namely, the sustainability function, as an aggregating metric. The results are qualitatively compared to those of the sustainability indexes proposed by Marteel et al. (2003).

ROUTE A was conceived in two alternative configurations: in classical arrangement (ROUTE A1), a PFR reactor is followed by a train of distillation columns; in ROUTE A2, a reactive distillation column with middle vessel arrangement is proposed. The analysis of both economical and environmental aspects shows that the reactive column configuration is more energy intensive, which leads to lower profit and higher environmental impact due to higher associated $CO_2$-eq emissions. Therefore, ROUTE A1 is more sustainable than ROUTE A2.

DMC life cycle was evaluated in two domains: gate-to-gate (from $CO_2$ reuse step to DMC production) and cradle-to-gate (raw materials production steps). When comparing routes' gate-to-gate domains, ROUTE A1 not only appears as the most sustainable option, but also consumes a higher amount of $CO_2$ (chemical capture) than ROUTE B: 36 Mg $CO_2$/year and 27 Mg $CO_2$/year, respectively. However, when expanding the $CO_2$-eq emission analysis to include cradle-to-gate domain, ROUTE B is shown to lower emission by a factor of 2.5 as compared to ROUTE A1. Nevertheless, Hossain et al. (2007) defends that the gate-to-gate domain should be given more relevance when comparing processes. This aspect was evaluated by modifying the proposed sustainability function to include cradle-to-gate domain.

ROUTE B has lower $EI^{ctg}$ but higher $EI^{gtg}$, which configures a conflict between the two domains. To trade-off among *P*, $EI^{ctg}$, and $EI^{gtg}$, weighting factors are used and a sensitivity analysis is performed. ROUTE A1 prevails as the most sustainable except when excessive weight is attributed to $EI^{ctg}$, in opposition to Hossain's recommendation. Last, to verify the results of the proposed methodology, metrics proposed by Marteel et al. (2003) were applied, indicating that ROUTE A1 presents better material index, energy index, and ecoefficiency.

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