What Horse to Bet on in CO_2 Utilization?
- An Assessment Case Study for Dimethyl Carbonate Production -

A. W. Zimmermann, R. Schomäcker[*]

[*]Technische Universität Berlin, Department of Reaction Engineering
Sekr. TC 8, Straße des 17. Juni 124, 10623 Berlin, Germany, arno.zimmermann@tu-berlin.de

ABSTRACT

CO_2 utilization is an emerging technology field, where technology assessment can contribute significantly to successful commercialization. However, current TEA lacks standardization. First, three indicators of a novel assessment framework are presented. Second, production routes of dimethyl carbonate are discussed, followed by an assessment of the routes. The urea route is identified as promising research direction.

Keywords: techno-economic assessment, CO_2 utilization, dimethyl carbonate, technology readiness level.

1 TECHNO-ECONOMIC ASSESSMENT OF CO_2 UTILISATION

1.1 Current state

Techno-Economic Assessment (TEA) plays an important role in the development of new technologies by providing recommendations for pathways to follow and allowing comparisons to commercial and even other emerging technologies. TEA is therefore a useful tool not only for researchers, but also for industry, funding agencies or politicians that are dealing with innovation.

CO_2 utilization is a technology concept with the aim of consuming CO_2 in order to make commercial products or services.[1] As many CO_2 utilization research projects are in the early stages of development,[2] TEA can be helpful in guiding future research. CO_2 utilization technologies often focus on large-scale industry solutions; their successful commercialization largely depends on a competitive cost-performance ratio. This is why a reliable estimation of cost and further feasibility factors, as well as adherence to a systematic assessment method, are crucial for future success.

In a recent literature review,[1] we showed that TEA in CO_2 utilization lacks standardization, thereby making results hard to compare. Furthermore, assessment often focused only on one or two of the four possible assessment fields (technologic feasibility, economics, environmental impact, and social impact).

In the following sections, we present excerpts of a novel assessment framework which could facilitate the evaluation of early-stage technologies by providing guidance and standardized indicators, enabling cross-technology comparison.

1.2 Development approach for novel assessment framework

The work on the assessment framework is currently ongoing. The findings presented in this paper are excerpts of the work in progress.

Four principles were considered during the development of this assessment framework: First, indicators were derived from a recent literature study[1] to ensure relevancy for research. Second, shortcut indicators are employed to overcome the typical high number of possible scenarios and uncertainties in assessment of early-stage technologies. Third, all technologies are compared on the same stage of maturity, based on the Technology Readiness Levels (TRL) concept,[3] to ensure a fair comparison. Fourth, the assessments are carried out in user perspectives: R&D (efficiency), industry (large-scale feasibility) and society/funding (risk), thereby integrating all four possible fields of assessment.

1.3 Example indicators

Three example indicators from the efficiency perspective are presented in the following: mass efficiency, value efficiency and CO_2 efficiency (see Table 1). The three indicators are presented for different maturity stages: TRL 2 (solutions creation) and TRL 4 (preliminary process engineering).[1] While TRL 2 only takes reaction equations and typical lab data into account (mass of reactants and products, enthalpy of reaction), TRL 4 uses process flow diagrams and includes mass flows $\dot{m}$, streams that are not recycled $\dot{m}_{demand}$ as well as additional streams that remain in the main product such as solvents $\dot{m}_{a,demand}$. The energy perspective is extended from enthalpy $\Delta H°$ in TRL 2 to exergy $\Delta \dot{b}$ in TRL 4.

Mass efficiency indicates the proportion of mass of all reactants m_r bound in the main product $m_{p,m}$ (similar to atom economy).[4] In TRL 4 this scope is extended from mass to mass flows.

Value efficiency measures the relative monetary value created or lost during the process. Prices of reactants π_r and additional inputs π_a as well as energy prices π_{energy} are compared to product prices π_p. Energy prices are only factored in for endothermic reactions, while the energy produced by exothermic reactions is not valuated. While in TRL 2 only one product price is considered, TRL 4

includes a price adaption for increased or decreased functionality (f), and sustainability (s).

CO$_2$ efficiency calculates the relative mass of carbon dioxide consumed in this process, setting it in relation to all reactants (TRL 2) and to additional streams (TRL 4).

Table 1. Efficiency indicators on TRL 2 and TRL 4.

Indicator	Equation
Mass eff. TRL 2	$\eta_{mass,TRL2} = \frac{\sum_{p,m} m_{p,m}}{\sum_r m_r}$
Mass eff. TRL 4	$\eta_{mass,TRL4} = \frac{\sum_{p,m} \dot{m}_{p,m,demand}}{\sum_r \dot{m}_{r,demand} + \sum_a \dot{m}_{a,demand}}$
Val. eff. TRL 2	$\eta_{val,TRL2} = \frac{\sum_p (m_p * \pi_p)}{\sum_r (m_p * \pi_r) + \Delta H° * \pi_{energy}}$
Val. eff. TRL 4	$\eta_{val,TRL4} = $ $\frac{\sum_p (\dot{m}_p \, (\pi_p + \pi_{p,f} + \pi_{p,s}))}{\sum_r (\dot{m}_{r,demand} * \pi_r) + \sum_a (\dot{m}_{a,demand} * \pi_a) + \Delta \dot{b} * \pi_{energy}}$
CO$_2$ eff. TRL 2	$\eta_{CO2,TRL2} = \frac{m_{r,CO2}}{\sum_r m_r}$
CO$_2$ eff. TRL 4	$\eta_{CO2,TRL4} = \frac{\dot{m}_{CO2,demand}}{\sum_r \dot{m}_{r,demand} + \sum_a \dot{m}_{a,demand}}$

In the following section this assessment framework is applied to a case study in CO$_2$ utilization. Five dimethyl carbonate production technologies are presented for the case study and assessed by the three indicators presented.

2 DIMETHYLCARBONATE CASE STUDY

2.1 Applications

Dimethylcarbonate (DMC) is an alkyl carbonate (CH$_3$O)$_2$CO, which is clear, flammable and liquid at room temperature. The main application of DMC is the production of polycarbonate (50% of 2014 market).[5,6] Other applications include solvents for paint and adhesives, non-aqueous electrolyte for lithium batteries, and pharmaceuticals. Furthermore, DMC could be useful in future fuel applications, mainly because of its rich oxygen content, low toxicity and good biodegradability.[7–9]

Currently the industrial production of DMC is carried out by three processes, which are discussed in the following section:
1. Eni process
2. Ube process
3. Asahi process

2.2 Current industrial production

The Eni process, introduced in the 1980s, is based on the liquid-phase partial carbonylation of methanol. It consists of three steps: a reaction step (in a slurry reactor), a gas separation step (gas recycling) and a product separation step (purification), see Figure 1.
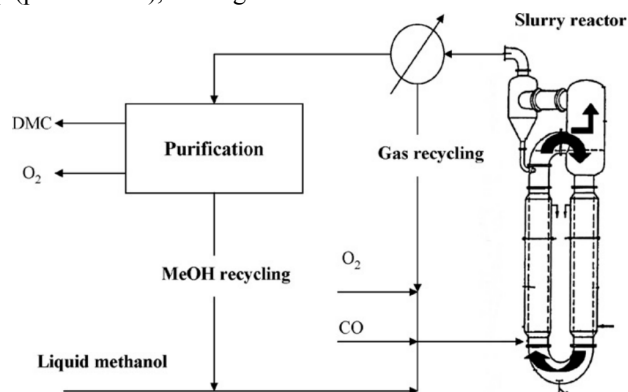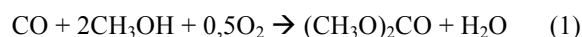

Figure 1. Eni process scheme, reprinted from Keller et al.[8] with permission from Elsevier.

Inputs for the DMC synthesis are carbon monoxide, methanol and oxygen; a resulting byproduct is water. The partial carbonylation reaction is carried out at 120-140°C and 20-40 bar, using a copper chloride (I) catalyst (see eq. 1).[8]

$$CO + 2CH_3OH + 0{,}5O_2 \rightarrow (CH_3O)_2CO + H_2O \qquad (1)$$

The product separation step (purification) remains challenging as DMC, methanol and water form two binary azeotropes.[9]

The UBE route was commercialized in the 1990s and is based on the gas-phase partial carbonylation of methyl nitrite. The process consists of two reactions; methyl nitrite synthesis and DMC synthesis, followed by a product separation step as shown in Figure 2.
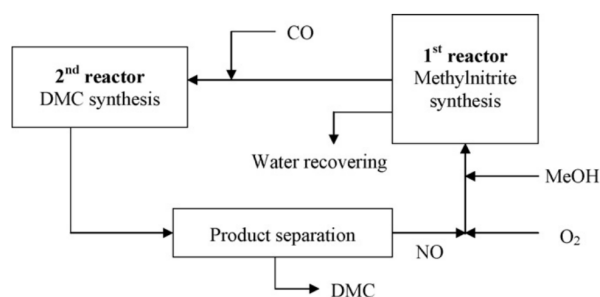

Figure 2. UBE process scheme, reprinted from Keller et al.[8] with permission from Elsevier.

The first reactor carries out the synthesis of methyl nitrite in the liquid phase at 60°C and without a catalyst. Nitrogen monoxide and oxygen first react to dinitrogentrioxide (N$_2$O$_3$) (eq. 2). Water is already separated after the first reaction to prevent the formation of an azeotrope.[8]

$$2NO + 0{,}5O_2 \rightarrow N_2O_3 \qquad (2)$$
$$2CH_3OH + N_2O_3 \rightarrow 2CH_3ONO + H_2O \qquad (3)$$

The second reactor carries out the synthesis of DMC in the gas phase, at 100-120°C and 5-10 bar, using an activated charcoal supported palladium chloride catalyst. Carbon monoxide and methyl nitrite serve as inputs for this reaction (eq. 4).

$$CO + 2CH_3ONO \rightarrow (CH_3O)_2CO + 2NO \qquad (4)$$
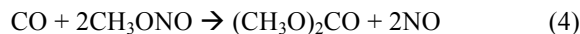
Following the DMC synthesis, the product stream is separated by an adsorption column.[8]

The Asahi process, introduced in the 2000s, is a production route for polycarbonate. It involves four reactions. In reaction 1, ethylene carbonate (EC) is produced from ethylene oxide (EO) and CO_2. In reaction 2, DMC and ethylene glycol (EG) are produced from EC and recycled methanol (MeOH). In reaction 3, diphenyl carbonate (DPC) and MeOH are produced from DMC and Phenol (PhOH); MeOH is recycled. In reaction 4, polycarbonate (PC) and PhOH are produced from DPC and Bisphenol-A (Bis-A); the PhOH is recycled. If seen individually, reaction 1 and reaction 2 (marked red) could be seen as CO_2-based DMC production. The Asahi process is run at 100-180°C and 40-60 bar (see Figure 3).[10,11]
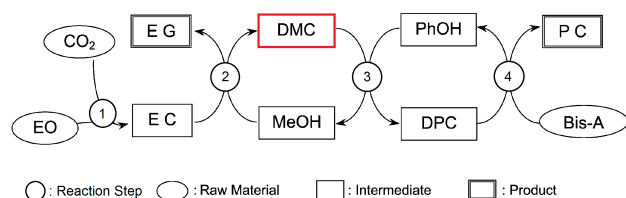

Figure 3. Asahi process scheme, adapted from Fukuoka et al.[10] with permission of the Royal Society of Chemistry.

The world market of DMC was estimated to 90 kt/a in 2002.[12] However, production figures are not widely available, and as DMC is also used as a production intermediate that is not sold on the market, the overall production of DMC is expected to be significantly higher.[7,13]

The major production route of "market DMC" in 2000 was the Eni process. The Ube route played a minor role, but major expansions plans were reported. As the phosgene route did not exhibit significant capacities - and is phased out in industry - it will not be discussed in this paper.[9,13,14]

As discussed, the ethylene carbonate route is an intermediate of the Asahi process for polycarbonate (PC) production. The overall Asahi route PC production capacities are estimated to 605 kt/a;[11] translating into a stoichiometric DMC production capacity of 105 kt/a.

A future use of DMC in fuel applications would require a substantial increase in production capacities, estimations reach from 0.5 kt/a[8] to 30 Mt/a.[15]

2.3 Further CO₂-based, alternative routes

The past has shown significant process innovations in DMC production every decade.[16] For the purposes of resource efficiency and green chemistry, two further production routes with the input carbon dioxide are discussed in research:
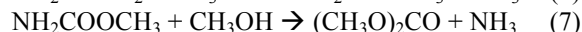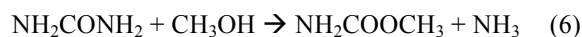1. the direct synthesis from CO_2,
2. the transesterification of urea.[8]

The direct synthesis route is based on a reaction of CO_2 and methanol, resulting in DMC and water (see eq. 5).

$$2CH_3OH + CO_2 \rightarrow (CH_3O)_2CO + H_2O \qquad (5)$$
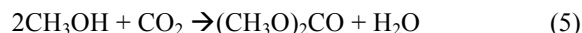
Reaction conditions are reported to range from 160-180°C, at 90-300 bar. Catalysts systems vary widely in current research. While this reaction concept would allow for the direct utilization of CO_2 without any harmful side products, it still suffers from several drawbacks. Major research challenges include the unfavorable thermodynamic conditions, kinetic inertness, the detrimental catalyst decomposition and the high effort of separation. A recent process simulation also shows that the separation makes reaction at current research state uneconomical and that conversion and separation has to be improved by the factor of 6 to 7.[8,17,18]

The urea route is a two-step reaction concept, starting from urea and methanol and resulting in DMC and ammonia (see eq. 6, 7).

$$NH_2CONH_2 + CH_3OH \rightarrow NH_2COOCH_3 + NH_3 \quad (6)$$
$$NH_2COOCH_3 + CH_3OH \rightarrow (CH_3O)_2CO + NH_3 \quad (7)$$

The first reaction is carried out at 100°C, while the second one required 180-190°C; the pressure conditions range from 1-30 bar. Both reactions are catalyzed by an equimolar mix of a lewis acid and a lewis base. Again, this reaction concept suffers from the drawback of unfavorable thermodynamic conditions. However product separation requires less effort compared to the direct synthesis route, as no azeotropes are formed.[8,17]

Other routes such as the transesterification of propylene oxide or electrochemical routes have been reported in industry and academic literature,[6,17] but are not part of current literature reviews and therefore excluded from the scope of this conference paper.

2.4 Assessment of DMC production routes

In the following, the three industrial routes and two research routes are assessed with the three presented indicators in the scope of TRL 2.

	Mass eff. TRL 2	Val. eff. TRL 2	CO_2 eff. TRL 2
Eni process	0.833	2.443	0
Ude process	0.833	2.443	0
Asahi process	0.750	1.803	0.366
Direct synthesis	0.833	2.698	0.407
Urea route	0.833	2.698	0.407

Furthermore process studies of the Eni process and of the Asahi process can be compared in the scope of TRL 4. Energy

	Mass eff. TRL 4	Val. eff. TRL 4	CO_2 eff. TRL 4
Eni process	0.730	2.353	0
Asahi process	0.400	1.116	0.272

2.5 Discussion and future work

As the overall reaction equations for the Eni and Ude process as well as for the direct synthesis and urea route are identical, the same values are calculated for the indicators of rows 1+2 and 4+5.

For TRL 2, the assessment does not show significant differences in mass efficiency. In terms of value efficiency, the direct synthesis and urea route equations reach the highest value. In terms of CO2 efficiency, the latter two processes also exhibit the highest performance.

For TRL 4 assessment, the values of all indicators decrease, as the additional mass and energy streams are considered. The Eni process shows higher values compared to the Asahi process.

Overall the Eni process route seems well suited for producing DMC for market sale. The Asahi routes shows lower mass and value efficiencies but makes the utilization of CO_2 possible. As the Asahi route is used for PC production, it is not in direct competition. Future research especially on the urea route makes sense as it shows even larger value efficiency than current industrial processes, while utilizing CO_2 and avoiding azeotropes.

The next steps are the completion of the method description in academic literature in combination with a case study with detailed process data.

REFERENCES

[1] A. W. Zimmermann, R. Schomäcker, *Energy Technol.* **2017**, DOI 10.1002/ente.201600805http://doi.wiley.com/10.1002/ente.201600805, accessed 16 March 2017.

[2] A. Zimmermann, M. Kant, R. Schomäcker, J. Kratzer, *Quo Vadis CO2 Utilisation? Definition and State of an Emerging Chemical Technology*, SCOT Final Conference, Brussels, Belgium, **2016**.

[3] J. C. Mankins, *Technology Readiness Levels A White Paper*, **1995**, https://www.hq.nasa.gov/office/codeq/trl/trl.pdf, accessed 23 March 2017.

[4] B. Trost, *Science (80-.).* **1991**, *254*, 1471–1477.

[5] Transparency Market Research, *Global Dimethyl Carbonate Market to Exhibit 6.6% CAGR 2015-2023 owing to Rising Demand for Polycarbonates and Paint and Coatings*, **2016**, http://www.transparencymarketresearch.com/pressrelease/global-dimethyl-carbonate-market.htm, accessed 29 March 2017.

[6] A. Coker, *Dimethyl carbonate*, **2013**, p. 7.

[7] C. B. Kreutzberger, in *Kirk-Othmer Encycl. Chem. Technol.*, John Wiley & Sons, Inc., Hoboken, NJ, USA, **2001**.

[8] N. Keller, G. Rebmann, V. Keller, *J. Mol. Catal. A Chem.* **2010**, *317*, 1–18.

[9] M. A. Pacheco, C. L. Marshall, *Energy & Fuels* **1997**, *11*, 2–29.

[10] S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa, S. Konno, *Green Chem.* **2003**, *5*, 497–507.

[11] I. Omae, *Coord. Chem. Rev.* **2012**, *256*, 1384–1405.

[12] F. Cavani, *Sustainable Industrial Processes*, Wiley-VCH, **2009**.

[13] H.-J. Buysch, in *Ullmann's Encycl. Ind. Chem.*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2000**.

[14] D. Delledonne, F. Rivetti, U. Romano, *Appl. Catal. A Gen.* **2001**, *221*, 241–251.

[15] E. A. Quadrelli, G. Centi, J.-L. L. Duplan, S. Perathoner, *ChemSusChem* **2011**, *4*, 1194–1215.

[16] M. Aresta, *Carbon Dioxide as Chemical Feedstock*, **2010**.

[17] I. Garcia-Herrero, R. M. Cuéllar-Franca, V. M. Enríquez-Gutiérrez, M. Alvarez-Guerra, A. Irabien, A. Azapagic, *ACS Sustain. Chem. Eng.* **2016**, *4*, 2088–2097.

[18] H. J. Kuenen, H. J. Mengers, D. C. Nijmeijer, A. G. J. van der Ham, A. A. Kiss, *Comput. Chem. Eng.* **2016**, *86*, 136–147.