**Analysis of the preferred ethylene production route from carbon dioxide at a supply chain level: results of mathematical modelling for a Teesside case study**

Grazia Leonzio,a,b\* Nilay Shahb

 aSargent Centre for Process Systems Engineering, Department of Chemical Engineering, Imperial College London, London SW7 2AZ, UK

 bDepartment of Mechanical, Chemical and Materials Engineering, University of Cagliari, via Marengo 2, 09123 Cagliari, Italy

\*grazia.leonzio@unica.it

Abstract

Currently, new routes for producing chemical building blocks are required with the aim to support the energy and feedstock transition. Considering both global demand and production capacity, ethylene is the most important organic chemical and for this reason alternative production routes (based on carbon dioxide and water) have been investigated and screened in terms of costs and emissions in one of our previous works. In this research, the best alternative ethylene production technology is suggested at a supply chain level for the Teesside cluster (UK) through the development of two different mathematical models for the supply chain. Results show that the best ethylene production route is based on methanol-to-olefin plant where methanol is produced by syngas obtained from carbon dioxide-water co-electrolysis. Through a global sensitivity analysis based on a surrogate model, it is found that the carbon dioxide utilization cost has the highest impact on the supply chain total cost. The optimization of the electrolytic cell could help with cost reduction.

**Keywords**: carbon dioxide, ethylene, supply chain, mathematical modelling, global sensitivity analysis.

* 1. Introduction

Nowadays there is a mismatch between the amount of carbon dioxide (CO2) that is emitted and the amount that is used, forcing researchers and companies to suggest new and alternative CO2 conversion routes to bridge this gap. Among different CO2-based products, ethylene is desirable due to its large market and has high value compared to other reduction products. For these reasons, new production systems have been proposed and investigated in the literature as in Ioannou et al. (2020) and Berkelaar et al. (2022). On the other hand, in one of our previous works we modelled and compared the cost and global warming potential of different ethylene production routes starting from CO2 and water (H2O) (Leonzio et al., 2023). Here, the investigated technologies are the following: the electrochemical process (tandem and direct CO2 electrochemical reduction to ethylene processes), methanol-to-olefin (MTO) plant with methanol obtained from CO2 hydrogenation with blue and green hydrogen and from CO2 electrochemical reduction, and MTO process with methanol obtained from syngas produced in a solid oxide electrolytic cell (SOEC) for the CO2-H2O co-electrolysis. We found that the electrochemical tandem process is the most promising from an economic point of view while the MTO process using methanol produced by syngas from CO2-H2O co-electrolysis in a solid oxide electrolytic cell (SOEC) is the most preferred from an environmental point of view.

After this first screening, in this research, we aim to explore the best route for ethylene production (between the two suggested above) at a supply chain level, by developing two different mixed integer linear programming (MILP) models for the supply chain located in the Teesside cluster (UK). Two different models are used to verify the independence of results by the used method. Through the development of a surrogate model, a Global Sensitivity Analysis (GSA) is conducted to determine the most significant factors for total cost and ethylene production cost.

* 1. Methodology
		1. Mathematical model of supply chain

In the considered supply chain, CO2 is captured from flue gas, transported via pipeline and stored/used for ethylene production through the two routes suggested in our previous work (Leonzio et al., 2023). Therefore, a carbon capture, utilization and storage (CCUS) supply chain is proposed here. In particular, the framework is located in the Teesside cluster (UK) where the Endurance reservoir is the CO2 storage site with a supposed storage capacity of 20 MtCO2. Companies like Sabic, Ineos, CF Fertiliser, Tioxide Europe and BOC Linde are the CO2 source sites, while the CO2 conversion site is set in the Sabic plant (Geels, 2022). Capture technologies like absorption with mono-ethanolamine, pressure and vacuum swing adsorption, membrane are taken into account. In that designed cluster, total CO2 emissions were 351.5 MtCO2 in 2019 and must be reduced by 54.8 % to achieve the target fixed for the future (2050) (Geels, 2022).

Two MILP models are developed to optimize the framework: one is based on a node structure as reported by Elahi et al. (2014) while the other one is non-node based as proposed by Leonzio et al. (2019). In both models, CO2 is flowing from sources to storage/utilization sites but in the first case a material balance is added as a constraint for each node.

The optimal topology is provided by the minimization of the total cost (e.g. the sum of CO2 capture and compression, CO2 transportation, CO2 storage and CO2 utilization costs) solved by using the AIMMS software tool with CPLEX 12.7.1 as the solver.

* + 1. Surrogate model

A surrogate model method used in the literature is the random sampling-high dimensional model representations (RS-HDMR) (Lambert et al., 2016), which is implemented here to express the supply chain total cost and ethylene production cost as a function of CO2 capture and compression cost, CO2 transportation cost, CO2 storage cost and CO2 utilization cost. The following equation (with 1 as the maximum grade for parameters β and α) is considered to be regressed (see Eq. 1):

$$F\left(x\right)=fo+α\_{1}^{cc}∙φ\_{1}\left(x\_{cc}\right)+α\_{1}^{ct}∙φ\_{1}\left(x\_{cT}\right)+α\_{1}^{cs}∙φ\_{1}\left(x\_{cs}\right)+α\_{1}^{cu}∙φ\_{1}\left(x\_{cU}\right)+$$

$$+β\_{1,1}^{cc,ct}∙φ\_{1}\left(x\_{cc}\right)∙φ\_{1}\left(x\_{cT}\right)+β\_{1,1}^{cc,cs}∙φ\_{1}\left(x\_{cc}\right)∙φ\_{1}\left(x\_{cs}\right)+β\_{1,1}^{cc,cu}∙φ\_{1}\left(x\_{cc}\right)∙φ\_{1}\left(x\_{cu}\right)+ $$

$$+β\_{1,1}^{ct,cs}∙φ\_{1}\left(x\_{ct}\right)∙φ\_{1}\left(x\_{cs}\right)+β\_{1,1}^{ct,cu}∙φ\_{1}\left(x\_{ct}\right)∙φ\_{1}\left(x\_{cu}\right)+β\_{1,1}^{cs,cu}∙φ\_{1}\left(x\_{cs}\right)∙φ\_{1}\left(x\_{cu}\right) (1)$$

with *F(x)* the supply chain total cost/ethylene production cost, *fo* a constant to be evaluated, *xcc*, *xct*, *xcs* *xcu* the uncertain variables respectively for CO2 capture and compression cost (cc), CO2 transportation cost (ct), CO2 storage cost (cs) and CO2 utilization cost (cu), α and β parameters to be found and$ φ\_{1}\left(x\_{i}\right)$ the Legendre orthogonal polynomial, as in Eq. (2) (Lambert et al., 2016):

$$φ\_{1}\left(x\_{i}\right)= \sqrt{3∙}\left(2∙x\_{i}-1\right) (2)$$

with i the each factor. In order to determine the value of each parameter, Sobol sampling (to generate 40 sampled points (Kleijnen, 2017)) is used for each factor which is varied between +/- 20 % of the base value according to a triangular probability distribution. For each input, the total cost and ethylene production cost are found through the supply chain optimization. The generated inputs and founded outputs are used to find the values of parameters through the software SobolGSA.

* + 1. Global sensitivity analysis

A GSA is carried out to quantify the overall uncertainty in a key performance indicator (KPI) by varying simultaneously all factors inside their uncertainty range. In this work, the supply chain total cost and ethylene production cost are the KPIs, while the CO2 capture and compression cost, CO2 transportation cost, CO2 storage cost and CO2 utilization cost are the considered factors. KPIs are evaluated through the developed surrogate models while each factor is taken into account through the respective Legendre orthogonal polynomial function for which 1,000 Sobol samples are considered for the uncertainty according to a triangular probability distribution (a range between +/- 20 % of the basic value is assumed for each factor) (Sobol, 2001). The GSA is developed by using the software tool SobolGSA, estimating total-order Sobol sensitivity indices.

* 1. Results and discussions
		1. Results of supply chain optimization

The optimization results show that, for both mathematical models, the best production route is based on the MTO plant with methanol from syngas because this is the only one selected for ethylene production. The supply chain cost is 5.9 $/kgEthylene and 5.7 $/kgEthylene for the models based on Leonzio et al. (2019) and Elahi et al. (2014) respectively. A sensitivity analysis is conducted changing the CO2 reduction rate and evaluating costs as in Figure 1: in both models, at a higher amount of captured CO2, the percentage of CO2 utilization cost on the total cost increases because at a fixed storage capacity more CO2 must be converted to achieve a higher reduction target.



Figure 1 Cost analysis of the CCUS supply chain in both models at different CO2 reduction rates

* + 1. Results of surrogate model

Through the software SobolGSA and according to the RS-HDMR method, the values of parameters for the surrogate models related to supply chain total cost and ethylene production cost are figured out as reported in Table 1. Data are shown here for both supply chain model structures.

Table 1 Values of parameters for CCUS supply chain surrogate models

|  |  |  |
| --- | --- | --- |
| Parameter | Non-node based structure | Node based structure |
| Total cost (k$/y) | Ethylene production cost ($/tEthylene) | Total cost (k$/y) | Ethylene production cost ($/tEthylene) |
| $$fo$$ | 430,338 | 6,019 | 333,754 | 5,778 |
| $$α\_{1}^{cc}$$ | 4,303 | 60.18 | 4,928 | 85.32 |
| $$α\_{1}^{ct}$$ | 3,963 | 55.43 | 479 | 8.29 |
| $$α\_{1}^{cs}$$ | -152 | -2.12 | 161 | 2.78 |
| $$α\_{1}^{cu}$$ | 23,049 | 322 | 18,670 | 323 |
| $$β\_{1,1}^{cc,ct}$$ | 411 | 5.75 | 331 | 5.73 |
| $$β\_{1,1}^{cc,cs}$$ | 276 | 3.85 | 290 | 5.02 |
| $$β\_{1,1}^{cc,cu}$$ | 618 | 8.64 | 507 | 8.77 |
| $$β\_{1,1}^{ct,cs}$$ | 1,255 | 17.55 | 860 | 14.88 |
| $$β\_{1,1}^{ct,cu}$$ | -243 | -3.39 | -337 | -5.83 |
| $$β\_{1,1}^{cs,cu}$$ | -598 | -8.36 | -317 | -5.49 |

* + 1. Results of global sensitivity analysis

Values of total-order Sobol sensitivity indices for each factor are reported in Table 2. A value higher than 0.05 makes the input significant (Zhang et al., 2015): only the CO2 utilization cost is significant for total and production cost in both supply chain models.

Table 2 Total-order Sobol sensitivity index for total cost/ethylene production cost for the supply chain and for each factor (1=CO2 capture and compression cost factor; 2=CO2 transportation cost factor; 3=CO2 storage cost factor; 4=CO2 utilization cost factor)

|  |  |  |
| --- | --- | --- |
| Sensitivity index | Non-node based structure | Node based structure |
| Stot[1] | 0.0075 | 0.0240 |
| Stot[2] | 0.0043 | 0.0029 |
| Stot[3] | 0.0059 | 0.0047 |
| Stot[4] | 0.9827 | 0.9688 |

According to this result, a sensitivity analysis is conducted keeping constant other cost factors and changing only the significant CO2 utilization cost factor in a range +/- 53 % of the base value by using the developed surrogate models. The analysis is carried out for both models to evaluate the specific cost ($/tCO2 avoided) with and without a carbon credit for the used CO2, as reported in Figure 2. According to the IPCC report, only technologies with CO2 abatement costs lower than 220 $/tCO2 avoided could be implemented by 2030 (Ostovari et al., 2023). Results show that at the base case, without carbon credit, only the non-node based model causes a supply chain total cost (228 $/tCO2 avoided) higher than that suggested by IPCC. On the other hand, the supply chain based on node modelling has a cost of 182 $/tCO2 avoided.



Figure 2 Total cost of CCUS supply chain changing the CO2 utilization cost factor compared to the base case in both models and the IPCC limit

In the first case, a reduction of CO2 utilization cost of about 20 % allows a total cost below the suggested limit. When a credit (45 $/tCO2 (Carbon Credit, 2023)) for only CO2 utilization is provided, both mathematical models at the base case ensure a total cost lower than that of the IPCC limit. In addition to the economic incentives, it is important to reduce the ethylene production cost so that, some suggestions are provided. It is needed to decrease the methanol production cost through the reduction of syngas production cost obtained by the SOEC. The highest influence of operating cost on methanol production through this route is reported by Adnan and Kribia (2020), while the high cost of syngas production through a SOEC is suggested by Redissi and Bouallou (2013). In a SOEC, operating costs have a great influence on total cost and the highest impact is due to the electricity cost (Freire Ordonez et al., 2021). For these reasons, further studies on SOECs should be conducted in order to improve Faradaic efficiency and current density and minimize the current leakage so that a lower power for syngas production will be needed. Low-cost and large-scale commercialization of SOECs requires a consistent current density higher than 5 A/cm, which is however hard to achieve, even for a high temperature electrolysis system (Cao et al., 2022). At this value of current density, a Faradaic efficiency of about 100% should be ensured so that the development of new catalysts and electrodes that are able to ensure this value is suggested. In addition to the above advice, lowering the temperature to a range of 500-700 °C could help in the reduction of maintenance costs by mitigating materials and maintenance issues. However, reducing the operating temperature decreases the electrocatalytic activity of electrode materials, requiring the development of high-performance materials.

* 1. Conclusions

Two different mathematical models (node and non-node based) are considered here for a CCUS supply chain producing ethylene. Different models are used in order to provide the independence of results from the model formulation. It is found that the best ethylene production route is based on the MTO plant, ensuring a cost of 5.9 $/kgEthylene and 5.7 $/kgEthylene respectively for the non-node based and node based models. A surrogate model is built with the RS-HDMR method to find through a GSA that, the most significant factor for cost is the CO2 utilization cost. In order to have the supply chain cost lower than the limit fixed by IPCC, more research and optimization should be conducted for the SOEC by improving current density and Faradaic efficiency.

**Acknowledgments:** Funding by the mobility of young researcher grant of Cagliari University and Imperial College London are gratefully acknowledged.

References

M.A. Adnan, M.G. Kibria, 2020. Comparative techno-economic and life-cycle assessment of power-to-methanol synthesis pathways, Appl. Energy 278, 115614

L. Berkelaar, J. van der Linde, J. Peper, A. Rajhans, D. Tiemessen, L. van der Ham, H. van den

Berg, 2022, Electrochemical conversion of carbon dioxide to ethylene: Plant design, evaluation and

prospects for the future, Chem. Eng. Res. Des., 182, 194–206

Carbon credit, 2023. Available at: <https://carboncredits.com/carbon-prices-today/>

J. Cao, Y. Li, Y. Zheng, S. Wang, W. Zhang, X. Qin, G. Geng, B. Yu, 2022, A Novel Solid Oxide

Electrolysis Cell with Micro-/Nano Channel Anode for Electrolysis at Ultra-High Current Density

pover 5 Acm−2, Adv. Energy Mater. 12, 2200899

D. Freire Ordonez, N. Shah, G. Guillen-Gosalbez, 2021, Economic and full environmental assessment of electrofuels via electrolysis and co-electrolysis considering externalities, Appl. Energy 286, 116488

N. Elahi, N. Shah, A. Korre, S. Durucan, 2014. Multi-period Least Cost Optimisation Model of an Integrated Carbon Dioxide Capture Transportation and Storage Infrastructure in the UK, Energy Procedia 63, 2655–2662

F.W. Geels, 2022, Conflicts between economic and low-carbon reorientation processes: Insights from a contextual analysis of evolving company strategies in the United Kingdom petrochemical industry (1970–2021), Energy Res. Soc. Sci. 91, 102729

I. Ioannou, S.C. D’Angelo, A.J. Martín, J. Pérez-Ramírez, G. Guillén-Gosálbez, 2020,

Hybridization of Fossil- and CO2-Based Routes for Ethylene Production using Renewable Energy,

ChemSusChem, 13, 6370–6380

J.P.C. Kleijnen, 2017, Regression and Kriging metamodels with their experimental designs in simulation: A review, Eur. J. Oper. Res., 256, 1, 1, 1-16.

R.S.C. Lamberta, F. Lemke, S.S. Kucherenko, S. Song, N. Shah, 2016, Global sensitivity analysis using sparse high dimensional model representations generated by the group method of data handling, Mat. Comp. Simul., 128, 42–54

G. Leonzio, B. Chachuat, N. Shah, 2023, Towards ethylene production from carbon dioxide: Economic and global warming potential assessment, Sustain. Prod. Consum. DOI:10.1016/j.spc.2023.10.015

G. Leonzio, F.U. Foscolo, E. Zondervan, 2019. Sustainable utilization and storage of carbon dioxide: Analysis and design of an innovative supply chain, Comput. Chem. Eng., 131, 106569

H. Ostovari, L. Kuhrmann, F. Mayer, H. Minten, A. Bardow. 2023. Towards a European supply chain for CO2 capture, utilization, and storage by mineralization: Insights from cost-optimal design, J. CO2 Util. 72, 102496

Y. Redissi, C. Bouallou, 2013, Valorization of Carbon Dioxide by Co-Electrolysis of CO2/H2O at High Temperature for Syngas Production, Energy Procedia 37, 6667 – 6678

I.M. Sobol, 2001, Global sensitivity indices for nonlinear mathematical models and their Monte Carlo estimates, Mathematics & Computers in Simulation 55, 271-280

X.Y. Zhang, M.N. Trame, L.J. Lesko, S. Schmidt, 2015. Sobol Sensitivity Analysis: A Tool to Guide the Development and Evaluation of Systems Pharmacology Models, CPT: pharmacometrics & systems pharmacology, 4, (2), 69–79.