

Document Version

Final published version

Citation (APA)

Manalal, J. T., Pérez-Fortes, M., Gonzalez, P. I., & Ramirez, A. R. (2023). Evaluation of alternative carbon based ethylene production in a petrochemical cluster: Technology screening & value chain impact assessment. In *Computer Aided Chemical Engineering* (pp. 2453-2458). (Computer Aided Chemical Engineering; Vol. 52). Elsevier. <https://doi.org/10.1016/B978-0-443-15274-0.50390-5>

Important note

To cite this publication, please use the final published version (if applicable). Please check the document version above.

Copyright

In case the licence states "Dutch Copyright Act (Article 25fa)", this publication was made available Green Open Access via the TU Delft Institutional Repository pursuant to Dutch Copyright Act (Article 25fa, the Taverne amendment). This provision does not affect copyright ownership. Unless copyright is transferred by contract or statute, it remains with the copyright holder.

Sharing and reuse

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights. We will remove access to the work immediately and investigate your claim.

Evaluation of alternative carbon based ethylene production in a petrochemical cluster: Technology screening & value chain impact assessment

James Tonny Manalal,^a Mar Pérez-Fortes,^a Paola Ibarra Gonzalez^a and Andrea Ramirez Ramirez^a

^a*Department of Engineering, Systems and Services, Faculty of Technology Policy and Management, Delft University of Technology, Jaffalaan 5, 2628BX, Delft, Netherlands.
E-mail: j.t.manalal@tudelft.nl*

Abstract

Due to the heavy dependence on fossil-fuels as raw materials, the defossilization of feedstocks in the petrochemical industry represents a challenge. A large number of possible process routes that use alternative carbon sources (ACS) like CO₂, biomass, and waste are being developed for the feedstock replacement. For instance, to produce ethylene, more than 40 ACS process routes were identified. These multiple options make the selection of the promising process route a complex task. By replacing feedstocks, a process can change significantly and the impacts related to these changes in a highly interconnected industrial cluster can create cascading effects due to system interdependencies. This work aims to understand the cascading impacts in carbon flows and prices of implementing an ACS production process in an ethylene cluster. The results show that PVC will be the highest impacted and defossilizing one value-chain can have cascading effect on other value-chains as observed for PET.

Keywords: technology screening, feedstock defossilization, alternative raw materials, value chain impacts.

1. Introduction

Europe has set the ambitious goal to be carbon-neutral by 2050 and feedstock defossilization of carbon-based industrial processes is challenging (J.Rissman et al, 2020). For instance, the petrochemical industry depends on fossil fuels like naphtha, natural gas and ethane as carbon sources. Using alternative carbon sources (ACS) such as CO₂, biomass and waste is considered an option for the replacement of oil and gas feedstocks (D. Saygain et al, 2021). A large number of possible processes using ACS are being developed to produce chemicals through electrochemical, biochemical, and thermochemical routes (M. Stork, 2018). The existence of multiple processing routes makes the decision-making process of selecting the promising alternative process route a complex task that relies on multiple techno-economic and environmental criteria. It can be expected that replacing feedstocks might significantly change process requirements like equipment, energy, water, utilities and safety, and production outputs like products, by-products, and waste. These changes can affect the overall system, for instance in terms of product prices and import-export dependencies, due to system interdependencies. This

work presents a systematic screening methodology for selecting promising ACS process technologies and aims to study cascading impacts (carbon and price), for the selected ACS ethylene production in an ethylene cluster as case study.

2. Methodology

For the production of ethylene using CO₂ and biomass as feedstocks, more than 40 different process routes were identified from the literature. In order to select the most promising alternative carbon-based ethylene production technologies a screening methodology was developed as explained in section 2.1. Then the value chain impacts of ACS technologies was studied for a base-case ethylene cluster, as explained in section 2.2 and section 2.3.

2.1. Technology screening

The screening methodology was developed based on a stage-gate concept and the selection was divided into five stages. The amount of information needed is reduced with this approach, as the processes are eliminated as stages progress. In stage-1, technology readiness level (TRL) is used for selection and technologies with TRL > 3 are selected to the next stage. In stage-2, the ideal stoichiometric reactions of each process route were used. Each stoichiometric reaction required to produce a chemical was assumed as individual unit operation or process step. Here, only ideal reactions are considered and side reactions are not taken into account. In stage-2, technologies with less than 4 process steps were selected. It was because as the number of steps increased, the number of routes as well as the level of complexity increased drastically. Then in stage-3, thermodynamic state functions; standard enthalpy change (ΔH^0), standard Gibbs energy change (ΔG^0) and standard entropy change (ΔS^0) for the overall reaction, were calculated at standard conditions using inputs from Aspen properties. Using these thermodynamic state functions, the theoretical overall heat need or generation and electricity need were calculated as:

$$\text{Heat production/need} = \sum_{\text{Biochemical+Thermochemical+Catalytic steps}} \Delta H^0 \quad (1)$$

$$\text{Electricity need} = \sum_{\text{Electrochemical step}} \Delta G^0 \quad (2)$$

At this stage, as the theoretical input and output components are known, the carbon utilization efficiency of the process route was calculated using Equation 3:

$$\text{Carbon utilisation efficiency (CUE)} = \frac{\text{Moles of carbon atom in product}}{\text{Moles of carbon atom in feedstock}} \quad (3)$$

Based on the energy need and CUE, technologies were then ranked. Using a comparative assessment, technologies with electricity need <1500 kJ/mol ethylene and CUE >50% were selected to the next stage. In stage-4, a basic economic constraint was calculated (Equation 4), using mass flow, component price and energy requirements. An in-house compiled price database with prices adjusted to 2018 as base-year using the PPI (producer prices indices) and price data from ICIS chemicals outlook was used.

$$\text{Economic constraint (EC)} = \frac{\sum_{\text{reactants}} \text{mass flow} * \text{Component price} + (\Delta H \text{ or } \Delta G)_{\text{endergonic}} * \text{Utility price}}{\sum_{\text{products}} \text{mass flow} * \text{Component price}} \quad (4)$$

Technologies with an economic constraint < 1 were selected. An EC ratio > 1 indicates that the input costs are higher than potential revenue and hence process is considered non-

profitable for assumed product prices. In stage-5, the process technologies which passed the previous gates were ranked based on the number of process steps and economic ratio, and one process route from each feedstock category (CO₂ and biomass) were selected.

2.2. Base-case ethylene cluster model

This paper used an in-house developed ethylene cluster model part of the project “Unravelling the impacts of using alternative raw materials in industrial clusters”, created in Aspen plus and based on existing processes in the Port of Rotterdam. The cluster model includes olefin, ethylene dichloride (EDC), vinyl chloride monomer (VCM), polyvinyl chloride (PVC), chlorine waste incineration (CKI), ethylene oxide (EO), ethylene glycol (EG), polyethylene terephthalate (PET), ethylbenzene (EB) and propylene oxide (PO)/styrene monomer (SM) synthesis units. The cluster has PVC, PET and SM value chains and these value-chains will be studied in this paper. The corresponding mass flows used as reference in this study are depicted in Figure 1.

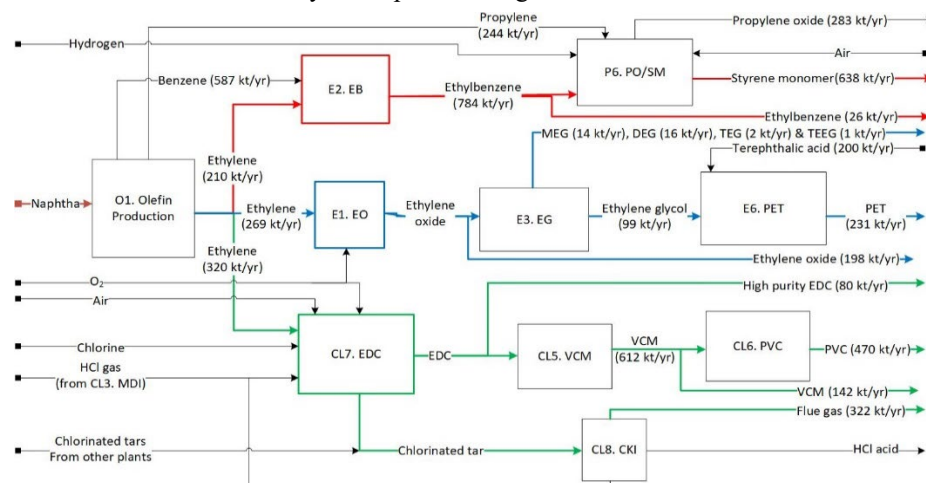


Figure 1: Simplified ethylene cluster with main mass flows

2.3. Value chain impact propagation

2.3.1. Feedstock defossilization impact on value chain

In this study, value chain defossilization is defined as the replacement of fossil-based raw materials with ACS carbon-based raw materials. To understand the extend of the defossilization impact on a value chain, Equation 5 and Equation 6 are used. The carbon contribution of a chemical building block (CBB) is defined as the amount of carbon in the value chain that originates from the CBB molecule (see Equation 5).

$$CBB \text{ carbon contribution} = \frac{CBB \text{ carbon atoms}}{\text{Value chain product carbon atoms}} \quad (5)$$

As in a chemical process, all the carbon used in a process does not end-up in the required product as by-products or waste are also formed. Hence, to understand the carbon flow along a value chain, the carbon utilization efficiency was also evaluated. The value chain carbon utilization efficiency (CUE) is defined as the ratio of the carbon mass flow in the value chain to the carbon mass flow of raw materials, as given in Equation 6. This equation helps to understand how efficiently the CBB carbon is used in the value chain to make the target product.

$$\text{Value chain CUE} = \frac{\text{Value chain chemical carbon mass flow}}{\sum_{\text{CBB}} \text{Carbon mass flow}} \quad (6)$$

2.3.2. Price change impact on value chain

It was assumed that the new ACS ethylene plant has the same capacity as the base-case ethylene production and the downstream units acquire the ethylene from the new ACS plant as it happens in the base-case scenario. For the downstream plants, it is considered their CAPEX remains the same (as the same product is produced and therefore there are no changes in equipment) but their OPEX changes due to changes in raw material price. Hence, in order to maintain the same gross margin, it is proposed that the downstream products will increase their corresponding prices (see Equation 7, and Equation 8).

$$\begin{aligned} \text{Gross margin} &= \text{Revenue}_{\text{base case}} - \text{OPEX}_{\text{base case}} = \\ &= \text{Revenue}_{\text{ACS case}} - \text{OPEX}_{\text{ACS case}} \end{aligned} \quad (7)$$

$$\sum_{\text{Products}} \Delta \text{Price} * \text{Mass flow} = \sum_{\text{Raw materials}} \Delta \text{Cost} * \text{Mass flow} \quad (8)$$

For multi-product processes, the increase in a raw material cost needs to be allocated to different products. In this study, a constant revenue ratio between products was assumed for all of them and, based on Equation 9, product prices were allocated.

$$\begin{aligned} &\left[\frac{\text{Product Price}_p * \text{Product mass flow}_p}{\sum_{\text{All products}} \text{Product Price} * \text{Product Mass flow}} \right]_{\text{base case}} \\ &= \left[\frac{\text{Product Price}_p * \text{Product mass flow}_p}{\sum_{\text{All products}} \text{Product Price} * \text{Product Mass flow}} \right]_{\text{ACS case}} \end{aligned} \quad (9)$$

3. Results and discussion

For the production of ethylene from CO₂ and biomass feedstocks, multiple technologies at different TRL were identified (see for example in Figure 2 the overview of CO₂-based routes).

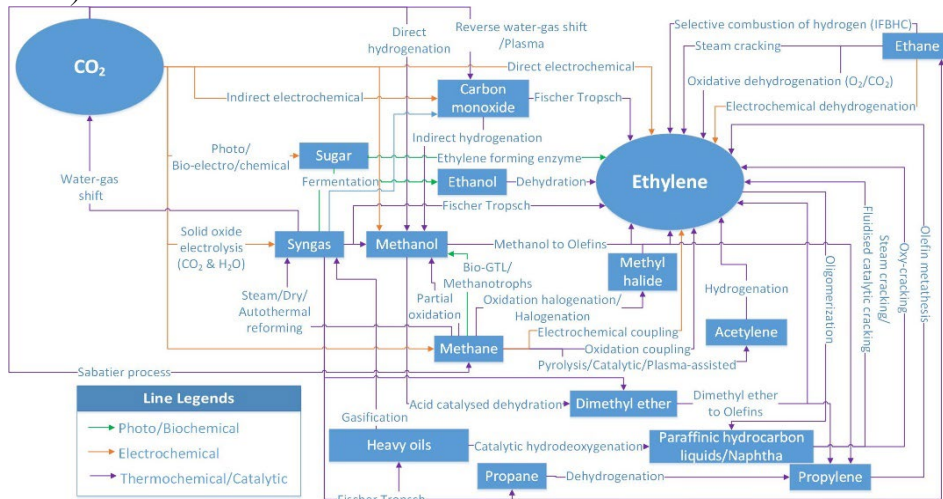


Figure 2: CO₂-based process routes for ethylene production

The identified technologies were evaluated using the screening methodology and a comparative assessment for a total of 48 process routes was performed (see for example in Table 1 the comparison of four process routes). It was observed that for CO₂-based routes, the needed theoretical electricity for the direct electrochemical route is lower than for the indirect water electrolysis route. This increase in electricity is reflected in the EC

ratio, as the input cost is higher in the indirect route. For biomass routes, there is no electrochemical process step and hence the electricity need is zero. But these routes have lower CUE than electrochemical routes as biomass does not have sufficient inherent H₂ for complete conversion of carbon in biomass. Hence, carbon is not fully utilized although these routes theoretically seem economically better than electrochemical routes because of their lower EC ratio. Hence, based on the screening methodology as explained in section 2.1 using criteria: number of process steps, energy usage, CUE and EC; the selected process routes for the production of ethylene from biomass and CO₂ feedstocks respectively were: Biomass steam gasification (BSG) with Fischer-Tropsch (FT) process and direct electrochemical reduction (DER) of CO₂ to ethylene.

Table 1: Process route comparison using the described screening methodology for ethylene production (Abbreviations: DER-Direct electrochemical reduction, MTO-Methanol to olefins, BSG- Biomass steam gasification, FT- Fischer Tropsch)

Technology	No. of process steps	kJ/mol ethylene		CUE	EC
		Electricity need	Heat production		
DER of CO ₂ to ethylene	1	1331	0	1.00	0.90
Water electrolysis + CO ₂ to methanol + MTO	3	1423	-304	1.00	0.95
BSG + FT process	2	0	-82	0.67	0.14
BSG + syngas to methanol + MTO	3	0	-82	0.67	0.14

In this paper, only downstream plant impacts are studied using the preliminary results. The defossilization impact of ACS ethylene on an ethylene cluster, were studied as explained in section 2.3.1 and the results are tabulated in Table 2. The PVC value chain had the highest carbon impact due to the ACS ethylene production, as 100% of PVC carbon comes from ethylene. The least carbon impact was found for PET value chain, as significant part of the carbon in PET is provided by xylene, not ethylene. Hence, the impact of ethylene defossilization is non-identical for different value chains, despite sharing the same CBB. It means that different value chains based on the same carbon contribution molecule may require different defossilization strategies. The value chain carbon utilization efficiency shows that in the PVC value chain, only 66% of the ethylene entering ends-up in the PVC product. The CUE varies for different value chains based on the main reaction selectivity, conversion, product recovery rate and by-product demand. The significance of by-product demand can be observed in the PET value chain as some of the ethylene entering is used to make ethylene oxide (EO) which is an intermediate product used in other value chains. Therefore, for multi-product value chains, the defossilization impact is not just limited to the target product but can have wider impact on other dependent value chains.

Table 2: Ethylene cluster carbon impact

Value chain	Value chain theoretical carbon flow	CBB carbon contribution	Value chain CUE
PVC	$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \xrightarrow{-HCl} C_2H_3Cl$	Ethylene= 100%	PVC= 66%, EDC=7%, VCM=20%, Waste=7%
PET	$C_2H_4 + 0.5 O_2 \rightarrow C_2H_4O + H_2O$ $\rightarrow C_2H_6O_2 + C_8H_6O_4$ $\rightarrow C_{10}H_8O_4 + 2H_2O$	Ethylene= 20% P-xylene= 80%	PET=33%, PTA=19%, EG=3%, EO= 25%, Waste=20%

SM	$C_2H_4 + C_6H_6 \rightarrow C_8H_{10}$ $\rightarrow C_8H_8 + H_2$	Ethylene= 25% Benzene= 75%	SM= 82% , EB= 3%, Waste=15%
----	---	---	---------------------------------------

The price impact of an ACS based ethylene plant on the value chains were studied as explained in section 2.3.2 and an ACS ethylene price increase of 67% was assumed as per literature (L.Berkelaar et al, 2022). As shown in Table 3, the PVC value chain will have the highest price impact due to the higher ACS ethylene price. This is because ethylene has the highest raw material purchase cost contribution in PVC due to its price and mass flow. However, in the PET and SM value chains, the respective product prices only increased by 17%. This is because ethylene is not the main raw material in these value chains, which can also be observed from the CBB carbon contribution values given in Table 2. This results also highlights how differently the price change impacts propagate in different value chains of the same CBB due to feedstock defossilization.

Table 3: Ethylene cluster price change impact

Value chain	Price change impact propagation (delta)
Ethylene→ EDC→ VCM→ PVC	67%→ 62%→ 62%→ 49%
Ethylene→ EO→ EG→ PET	67%→ 47%→ 47%→ 17%
Ethylene→ EB→ SM	67%→ 17%→ 17%

4. Conclusion

A screening methodology based on stage-gate concept was developed to select promising ACS technologies for ethylene production. From 48 process routes, the selected technologies were: DER (for CO₂ feedstock) and BSG with Fischer Tropsch (for biomass feedstock). The methodology showed how the concept of stage-gate can be used to screen large number of process routes. Then the value chain impacts of feedstock defossilization for an ethylene cluster in terms of product carbon flow and price change was studied. It was observed that for ethylene value chain, PVC will have the highest carbon and price impacts due to the mass and price significance of ethylene in PVC production. It was also observed that as in the case of PET value chain, how defossilization of one value chain can effect multiple value chains due to system interdependencies.

Acknowledgements

This publication is part of the project Unravelling the impacts of using alternative raw materials in industrial clusters (with project number VI.C.183.010) of the research programme Vici DO which is (partly) financed by the Dutch Research Council (NWO).

References

- J. Rissman et al., "Technologies and policies to decarbonize global industry: Review and assessment of mitigation drivers through 2070," *Appl. Energy*, vol. 266, no. March, p. 114848, May 2020, doi: 10.1016/j.apenergy.2020.114848.
- D. Saygin and D. Gielen, "Zero-Emission Pathway for the Global Chemical and Petrochemical Sector," *Energies*, vol. 14, no. 13, p. 3772, Jun. 2021, doi: 10.3390/en14133772.
- M. Stork, J. de Beer, N. Lintmeijer, and B. den Ouden, "Chemistry for Climate: Acting on the need for speed. Roadmap for the Dutch Chemical Industry towards 2050," *Vnci*, pp. 1–52, 2018.
- L. Berkelaar et al., "Electrochemical conversion of carbon dioxide to ethylene: Plant design, evaluation and prospects for the future," *Chemical Engineering Research and Design*, vol. 182, pp. 194-206, 2022, doi: 10.1016/j.cherd.2022.03.034