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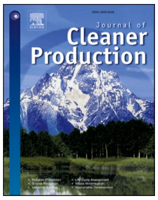

Assessing impacts of deploying bio-based isobutene for MTBE production in an existing petrochemical cluster

Inna Stepchuk [a,*], Mar Pérez-Fortes [a], Andrea Ramírez [b]

[a] Department of Engineering Systems and Services, Faculty of Technology, Policy and Management, Delft University of Technology, Jaffalaan 5, 2628 BX, Delft, the Netherlands
[b] Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, Van der Maasweg 9, 2628 CN, Delft, the Netherlands

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ABSTRACT

Alternative carbon sources (ACS) are increasingly considered necessary for the defossilisation of fossil-based chemicals. However, the potential and impacts of integrating ACS-based processes in existing petrochemical clusters are often overlooked. This paper aims to systematically analyse key techno-economic and environmental indicators associated with producing bio-based isobutene as an option to defossilise the production of methyl-tert-butyl-ether (MTBE) in the Port of Rotterdam, the Netherlands. The assessment is conducted at process and cluster levels. For this, the bio-isobutene (bio-IBN) process (358 kt/y of product), along with the existing fossil-based processes involved in MTBE production (i.e. the MTBE cluster), were modelled in Aspen Plus v12. The results show that under current conditions, although bio-IBN production could defossilise the MTBE cluster by c.a. 80 %, it is not cost-competitive compared to the current fossil-based process. Furthermore, deploying the bio-IBN process would significantly change the structure of the existing MTBE cluster, increasing by a factor of two or larger electricity, cooling water and bare land requirements. These requirements would affect the economic and environmental performance of the full cluster. The results emphasise the critical role of strategic change of new processes within existing petrochemical clusters.

Abbreviations:

ACS	Alternative carbon sources
APEA	Aspen process economic analyser
Bio-IBN	Bio-isobutene
CAPEX	Capital expenditures
CBBs	Chemical building blocks
CHP	Combined heat and power
CO_2	Carbon dioxide
CW	Cooling water
HGU	Heat generation unit
HPs	Heat pumps
HPS	High-pressure steam
LLPS	Very low-pressure steam
LPS	Low-pressure steam
MEUR	Million EUR
MPS	Medium-pressure steam
MSP	Minimum selling price
MTBE	Methyl tert-butyl ether
OPEX	Operational expenditures
PJ	Peta joules
PO	Propylene oxide
PoR	Port of Rotterdam
SI	Supplementary information
TBA	Tert-butyl alcohol
TEE	Techno-economic and environmental
TJ	Tera joules
TRL	Technology readiness level
TWC	Total water consumption
VC-HP	Vapour compression heat pump

1. Introduction

Methyl tert-butyl ether (MTBE) is a commonly used downstream derivative (DD) produced in the chemical industry. It has several applications, including its use as a fuel oxygenate in the automotive industry and as a solvent for medical and laboratory applications in the pharmaceutical industry (Wright, 2018). Its production worldwide exceeds 35 million metric tonnes, with an expected growth of 6 % by 2028

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* Corresponding author.
E-mail address: i.stepchuk@tudelft.nl (I. Stepchuk).

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(Statista, 2023), despite its prohibited use in various countries (Research and Markets, 2020). In Europe, the MTBE industry has faced the elimination of MTBE imports from Russia, which likely means that Europe will keep its production in the short and medium term. Furthermore, the use of bio-MTBE currently counts towards biofuel mandates in most European countries (Argus, 2023). In 2018, the total MTBE production in the Port of Rotterdam (PoR), the Netherlands, reached 0.86 million metric tonnes, accounting for nearly 43 % of European MTBE production (Wright, 2018). In this site, propylene oxide (PO) and tert-butyl alcohol (TBA) are also produced, which are the precursors of MTBE (de Haas and van Dril, 2022).

Conventionally, MTBE is produced from fossil-based sources in two pathways: (i) blending isobutene and methanol over a catalyst bed or (ii) dehydrating TBA in the presence of methanol (Wright, 2018) (i.e., the route used in the PoR (Yong and Keys, 2021). To defossilise the current production of MTBE, it is required to change the origin of the carbon entering the process by employing alternative carbon sources (ACS), such as biomass, waste, and carbon dioxide, and this can be done by defossilising methanol and or isobutene. Existing research has focused on using ACS to produce chemical building blocks (CBBs) (e.g., bio-methanol, bio-ethanol, syngas), which then can be used as the basis for defossilising MTBE production (see Fig. 1). However, to the authors' knowledge, no direct routes from ACS are reported in the literature for MTBE production.

The most common ACS-based pathway found in literature is the use of bio-methanol to produce ACS-based MTBE (SABIC, 2021). However, this pathway still requires the use of fossil-based isobutene, which represents about 80 % of the total carbon feedstock present in MTBE. Therefore, the complete defossilisation of MTBE would require all feedstocks containing non-fossil carbon, including isobutene. In recent years, isobutene production from ACS has shown a growing interest among companies, as illustrated by the demonstration projects launched by Global Bioenergies (fermentation of sugars into isobutene (Bailey, 2022)) and Optisochem (hydrolysate fermentation into isobutene (Optisochem, 2022)). Moreover, ongoing research for other emerging ACS-based routes can also be found in the literature (e.g., mevalonate pathway or Aldol condensation coupled with dehydration, as shown in Fig. 1). According to (Moncada et al., 2017) and (Wilson et al., 2018),

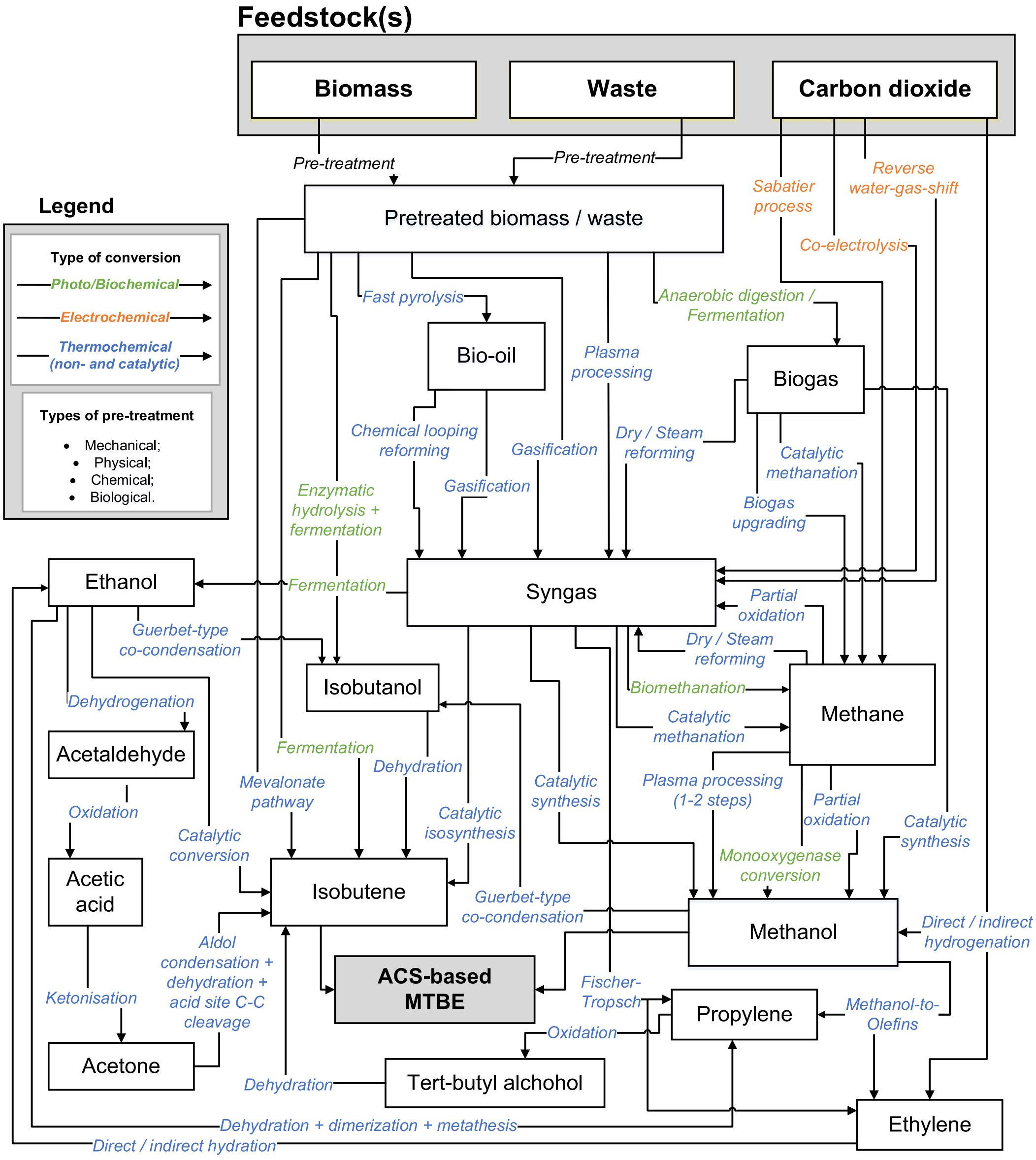


Fig. 1. Overview of ACS-based MTBE production pathways. The conversion categories are indicated in green, orange and blue. A list of carbon sources and processes can be found in Appendix A, supplementary information file, Table S.1.

one of the most common ACS-based pathways to produce isobutene is the dehydration of isobutanol produced through enzymatic hydrolysis and sugar fermentation. Thus, this work employs the following route to explore its potential and performance to defossilise the existing MTBE production.

To produce isobutene from sugars, a pre-treatment stage is required to break biomass into cellulose, hemicellulose and lignin (Thuijl et al., 2003). The majority of the research focuses on steam explosion (Ziegler-Devin et al., 2021), dilute-acid (Humbird et al., 2011) and organosolv pre-treatment (Wildschut et al., 2013). Organosolv (i.e., technology readiness level (TRL) 7) has found a growing interest among biorefineries, despite its drawbacks (i.e., energy intensity and costs), as the process extracts high-quality streams, allowing to reutilise them in the production of other downstream chemicals (e.g., ethanol, furfural, hydroxymethylfurfural) (Rabelo et al., 2023). After the pre-treatment, the extracted sugars are fermented into highly dilute isobutanol, which must be further separated from water to be converted into isobutene. Purifying dilute isobutanol is still a complex and costly downstream separation process (Janković et al., 2024). Despite that, the fermentation process is employed by the producers in the US (i.e., Gevo Inc. and Butamax Advanced Biofuels LCC) and Europe (i.e., Abengoa, Eastman Chemical Company (Grand view research, 2022). Among a variety of downstream separation technologies present in the literature (e.g., gas stripping and vacuum evaporation, supercritical extraction, membrane extraction, etc. (Fu et al., 2021)), it is reported that the dehydration of isobutanol to isobutene is a promising and relatively well-established process (i.e., TRL 6–7) (Tian et al., 2021).

Ex-ante technology assessments are often used to compare the potential performance of novel ACS-based routes with their fossil-based counterparts. Most of them focus on comparing the techno-economic and environmental (TEE) performances of stand-alone ACS-based and fossil-based processes (Roes and Patel, 2011) based on the information obtained from process modelling (van der Spek et al., 2017). In most cases, they assess processes for CBBs production while overlooking or underestimating the downstream process requirements (Posada et al., 2013). This is one of the visible drawbacks, as, in the case of the MTBE, ACS-based routes involve the production of new intermediate chemicals (e.g., isobutanol), thereby avoiding or decreasing the use of current CBBs (Moncada et al., 2015). Thus, ex-ante assessments are required to be adapted and tested for evaluation of ACS-based DD production. Another drawback of these assessments is that they lack evaluation of the impacts beyond the boundaries of the process, thereby neglecting the fact that the vast majority of the chemicals produced today are interconnected in (already existing) clusters through energy, mass and/or waste flows (Porter, 1998). Such interactions, while allowing current industrial clusters to increase energy and material efficiencies, also make individual processes harder to defossilise (Saygin and Gielen, 2021), as any change in processes could cause direct or indirect impacts on the cluster level (Boons et al., 2011). However, to the authors' knowledge, these aspects remain highly unexplored in literature. There is a strong need to obtain more realistic insights into the performance and impacts of ACS-based technologies after the deployment; it is important to identify and evaluate such (positive or negative) impacts.

This paper aims to identify and analyse the impacts of deploying a bio-IBN production process for the defossilisation of MTBE production in an existing cluster. To achieve this, the goal is split into two sub-goals to assess the impacts at two levels. First, to assess and compare the techno-economic and environmental performance of the bio-IBN process and its fossil-based counterpart. Second, to evaluate its performance and impact on MTBE production (i.e., the MTBE cluster) after its deployment, using the Port of Rotterdam as a case study. The originality of this research is rooted in assessing impacts at the cluster level of changing production processes already embedded in existing petrochemical clusters and are highly symbiotic in mass and energy flows. Compared to other works where green fields are assumed, this research includes the real constraints of brown industrial fields. In addition, the study focuses on DD production, which, compared to the production of CBBs, is generally overlooked as an option for defossilisation.

2. Materials and methods

The methodological approach followed in this paper consisted of four main steps: (i) scope definition and system boundaries; (ii) model development; (iii) assessment of the performance of the bio-IBN and fossil-based isobutene production processes; and (iv) assessment of the impacts associated with the introduction of the bio-IBN production process within an existing MTBE cluster.

2.1. Scope definition and system boundaries

The study focused on the production of isobutene from an ACS-based feedstock (i.e., biomass) as a part of the MTBE cluster. The research uses, as a point of departure, the production of MTBE in an in-house model, which was developed based on the existing industrial cluster of the Port of Rotterdam, the Netherlands. The model contains 52 processes modelled in Aspen Plus v12 and mimics existing interconnections in mass and energy inside the petrochemical cluster (for further information on the in-house model, see (Tan et al., 2024)).

In the current study, two system boundaries were differentiated: process and cluster (see Fig. 2). The process boundary that included the stand-alone production process of isobutene (i.e., (i) fossil-based IBN process in dark grey, Fig. 2a; and (ii) bio-IBN process in Fig. 2b) was used in the assessment and comparison of the TEE performance of the production processes (see Section 3.1). The cluster boundary (i.e., the MTBE cluster, Fig. 2) considered all upstream and downstream processes involved in the MTBE production and was used to assess the performance and structural changes associated with integrating the bio-IBN process into the existing MTBE cluster (see Section 3.2). It is important to note that the processes (white boxes in Fig. 2a) are parts of different companies in the cluster.

The current production capacity of fossil-based isobutene in the PoR is 358 kt/y at 99 % wt in purity, of which 261 kt/y is used to synthesise 400 kt/y of MTBE, while the remaining 97 kt/y are assumed to be sold to the market (i.e., it is not used as an intermediate in any other process in the cluster). The same production capacity was adopted for modelling the ACS-based process. For both models (fossil and ACS), the required material inputs (e.g., feedstocks and auxiliary chemicals) were bought from the market. Mimicking the existing situation in the PoR, utilities (e.g., steam, electricity) were first generated within the production process(es) and reused wherever possible in the process and/or the cluster. If additional utilities were required, they were assumed to be bought from (or sold in) the market. Flue gasses from internal heat generation processes were cleaned prior to their release into the atmosphere. Furthermore, although heat integration of the full process was outside the scope of the current study, the pinch point analysis was used (based on Aspen Energy Analyzer – AEA) to identify the most significant heat exchanges and minimise external utility needs. Hazardous and waste liquid streams were assumed to be sent to treatment facilities, which were considered outside of the system boundaries of the study and thus only included as operating costs. By-products were directly sent to the next production facility (if possible) or sold to the market (i.e., no storage facilities were included).

2.2. Model development

2.2.1. Process modelling

Fig. 2 depicts the main processes in the fossil-based MTBE cluster and bio-IBN production. The processes (fossil- and ACS-based) were assumed to operate 8000 h/y, for further details (i.e., data collection, modelling assumption) refer to Table 8. A detailed description of the fossil- and bio-IBN production processes, together with their process flow diagrams (PFDs), can be found in Appendix A, supplementary information (SI)

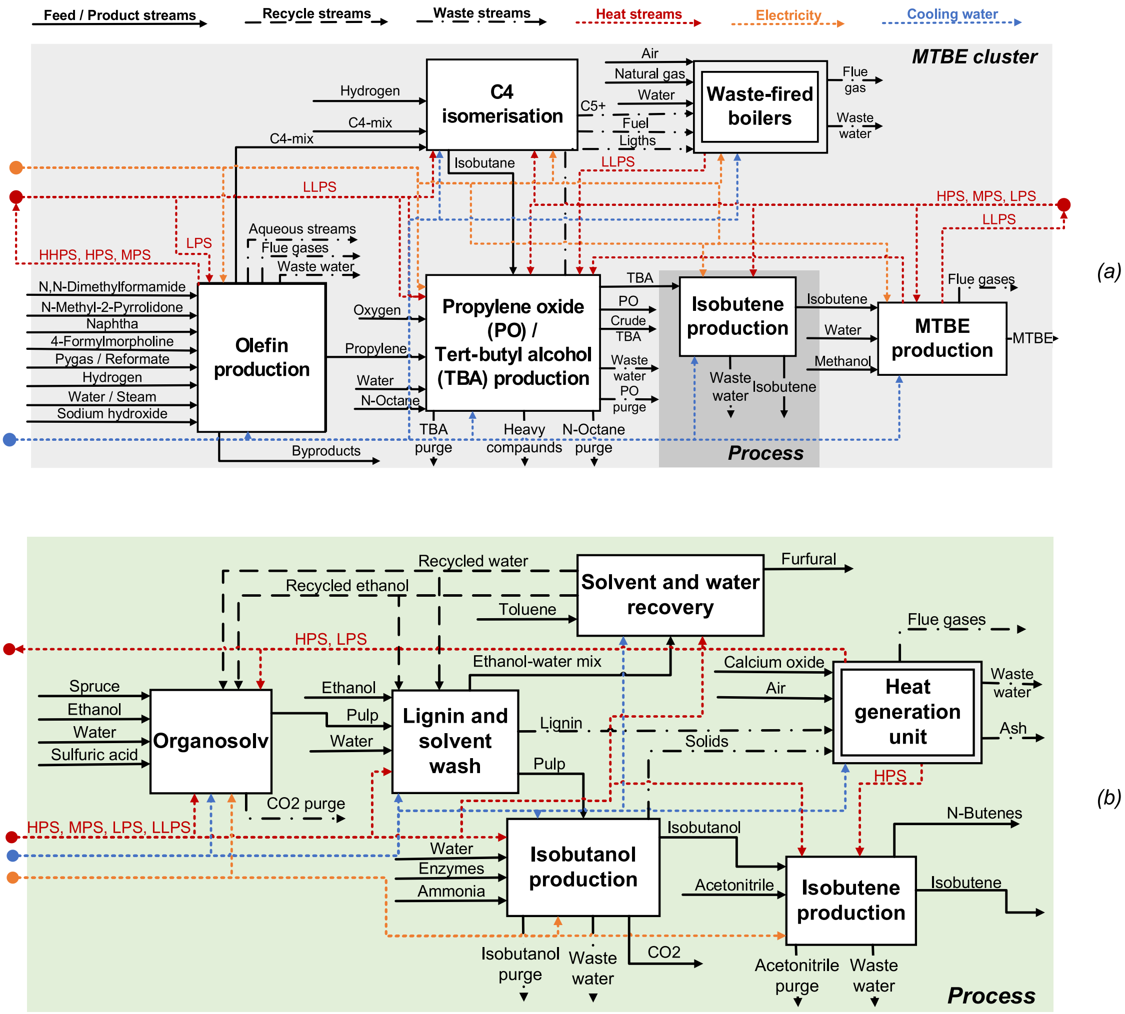


Fig. 2. Block diagrams: (a) MTBE production in the current fossil-based cluster and (b) ACS-based isobutene production process. LLPS – very low-pressure steam; LPS – low-pressure steam; MPS – medium-pressure steam; HPS – high-pressure steam.

file.

For the bio-IBN model, the biomass composition and the process description to convert biomass into isobutanol were taken from (Constant et al., 2016) and (Moncada et al., 2017). Missing properties (i.e., enthalpy of formation, molar mass of the components) for biomass components (i.e., sugars, xylose) were retrieved from the National Institute of Standards and Technology (NIST). Additionally, for non-conventional components (i.e., cellulose), properties modules (i.e., INHSPCD) were imported into Aspen Plus v12 (Wooley and Putsche, 1996). Multiple property methods were used in both simulations (for further information, see Table 8). The selection of property methods followed the methodology proposed in (Carlson, 1996).

2.2.2. Modelling assumptions and validation

The fossil- and ACS-based processes were modelled using similar approaches for the reaction, separation, and recovery sections. The reaction sections were modelled using RStoic reactors based on chemical kinetics. The separation and recovery sections were modelled using (i) RadFrac columns for liquid separation (i.e., defined based on shortcut distillation model DSTWU and/or literature data), (ii) filters and centrifuges, CFuge, for solids, and (iii) flashes and decanters for easily-separable mixtures (i.e., different phases and/or densities), respectively. Pumps, compressors (i.e., Compr or MCompr), and valves were used for pressure changes. Heaters and HeatEX were used for heating and cooling. For the bio-IBN process model, when data was unavailable, an ideal separation was modelled using a Sep model. This was, however, the case in less than 5 % of the total equipment modelled. The characteristics (i.e., pressure, temperature, vapour fraction) of the utility streams (i.e., steam, cooling, chilling) are shown in Appendix A, SI file, Table S.3.

For model validation, when possible, the model results were compared to data from open sources, see Table 8. Due to the lack of data for the whole bio-IBN production process, the validation was done only for the individual process units for isobutene production (i.e., organosolv process, isobutanol production, isobutene production). In the case of the fossil-based process, results were validated by comparing them with the data from the existing processes in terms of mass and energy consumption per amount of product.

The downstream separation units of the bio-IBN process were modelled using fractional distillation (i.e., based on their different boiling temperatures). For distillation units (ethanol-water), a vapour compression heat pump (VC-HP) (Kiss et al., 2012) was proposed to improve the heating and cooling requirements of the units (see Appendix A, SI file). For this, additional capital expenditures (CAPEX) associated with installing the VC-HP units were based on (De Raad et al., 2023) and (TNO, 2024).

2.3. Performance assessment of the ACS- and fossil-based isobutene production processes

2.3.1. Techno-economic and environmental assessments and comparison

The performances of the fossil- and bio-IBN processes were assessed using the TEE indicators described in Table 1, based on the data retrieved from the models (see Table 8). For assessing the economic performance, bare equipment costs were taken from the Aspen Plus economic analyser, and raw material prices were obtained from the literature. Market prices of materials and utilities (see Appendix A, SI file, Table S.2 and S.3) were gathered for various years and were harmonised to the same currency and year (EUR and 2018) using the Producer Price Index for the Chemical industry (CPI index) (FRED, 2024). The year 2018 was chosen to avoid fluctuations in market prices induced by the COVID-19 lockdowns. When needed, economic allocation was applied based on the price of the products, by-products or utilities (Manalal et al., 2023). For the analysis, a payback period of 12 years, plant lifetime of 25 years, interest rate of 8 % and a tax rate of 25 % were assumed.

The environmental performance was evaluated by assessing the water consumption, bare land requirements, and CO_2 emissions at Scope 1 (process) and Scope 2 (energy-related CO_2 emissions). For Scope 2, emission rates (see Appendix A, SI file, Table S.4) were estimated using economic allocation based on the retrieved data (i.e., stream compositions) from the Aspen Plus models of the utility units (i.e., natural gas and waste-fired boilers and combined heat and power plants (CHPs)) in

Table 1
List of the techno-economic and environmental indicators used for performance assessment. Applicable to process and cluster levels.

Indicator	Definition	Formula	Data inputs	Ref.
Techno-economic				
Carbon feedstock	The total mass of carbon in material flows of feedstocks.	$C_f = \sum_{i=1}^{n} m_i^{in} \cdot C_{wt\%_i}$	• m_i^{in} – mass of material entering the production process, kt/y; • $C_{wt\%_i}$ – weight percent of the carbon in the chemical, wt%.	(Stepchuk et al., 2023)
Net energy/power	The sum of energy flows of utilities used and generated in the process.	$TEC = \sum_{i=1}^{n} E_i^{in} + \sum_{i=1}^{n} E_i^{out}$	• E_i^{in} – energy/power used in the production process, TJ/y; • E_i^{out} – energy/power excess in the production process, TJ/y.	(Ruiz-Mercado et al., 2012)
Capital expenditures	The sum of investments required.	$CAPEX = ISBL + OSBL + ECC + CC + WC$	• $ISBL$ – inside battery limits (bare equipment costs), MEUR; • $OSBL$ – offsite battery limits, includes the costs of the additions (f.e. the site infrastructure); ∼(0.3–0.4)*$ISBL$, MEUR; • ECC – engineering and constructions costs; ∼(0.25–0.3)*$ISBL$, MEUR; • CC – contingency chargers ∼0.1*$ISBL$, MEUR; • WC – working capital ∼0.15*$ISBL$, MEUR.	(Towler and Sinnott, 2013)
Operational expenditures	The sum of the annual operating expenses.	$OPEX = VCOP + DCOP + OCOP$	• $VCOP$ – variable costs of production, MEUR/y; • $DCOP$ – direct costs of production, MEUR/y; • $OCOP$ – other costs of production, MEUR/y.	(Towler and Sinnott, 2013)
Equivalent annual operating costs	The combined CAPEX and OPEX presented in a single cash annual equivalent amount.	$EAOC = OPEX + \frac{CAPEX \cdot i \cdot (1+i)^{sl}}{(1+i)^{sl} - 1}$	• sl – total number of years of service life, assumed 25 years; • $CAPEX$ – capital expenditures, MEUR; • $OPEX$ – operational expenditures, MEUR/y; • i – interest rate, assumed 8 %.	(Turton et al., 2009)
Minimum selling price	The sale price of a product determined at the break-even point.	$MSP = Revenue/_{m_{prod}}$	• $Revenue$ – the income generated from all sales of goods, MEUR/y.	–
Environmental				
Total water consumption	The amount of water permanently removed from the water source, including water losses due to utility usage.	$TWC = \sum_{i=1}^{n} m_{w_i}^{in} + \sum_{i=1}^{n} k_{steam} \cdot m_i^{steam} + \sum_{i=1}^{n} k_{CW} \cdot m_i^{CW} - \sum_{i=1}^{n} m_i^{WW}$	• m_{wi}^{in} – mass of process water entering the production process, kt/y; • k_{steam}– coefficient for steam loss, assumed 25 %; • m_i^{steam} – mass steam used in the production process, kt/y; • k_{CW} – coefficient for cooling water loss, assumed 2 %; • m_i^{CW} – mass steam used in the production process, kt/y; • m_i^{WW} – mass of waste water exiting the production process, kt/y.	(ARI-Armaturen GmbH & Co. KG, 2018; UNEP, 2016)
Total bare land requirement	The sum of land footprint occupied by the total equipment.	$TL = \sum_{k=1}^{n} A_k$	• $k = (1 \ldots n)$– number of equipment used in the production; • A_k – bare equipment area, m^2.	–
Scope 1: Process-related CO_2 emissions	The sum of direct emissions associated with a production process.	$CO_2^{scope1} = \sum_{j=1}^{n} {CO_2}_j^{out}$	• $j = (1 \ldots n)$– number of gaseous waste streams exiting production; • ${CO_2}_j^{out}$ – emissions associated with the waste stream, kt CO_2-eq/y.	–
Scope 2: Energy-related CO_2 emissions	The sum of indirect emissions associated with the utilities required for the production process.	$CO_2^{scope2} = \sum_{u=1}^{n} {CO_2}_u^{out}$	• $u = (1 \ldots n)$– number of utility flows entering the production; • ${CO_2}_j^{out}$ – emissions produced from utilities used, kt CO_2-eq/y.	–
Total CO_2 emissions	Total emissions from the production process: Scope 1 and 2.	$CO_2^{total} = CO_2^{scope1} + CO_2^{scope2}$	• CO_2^{scope1}– emissions (Scope 1), kt CO_2-eq/y; • CO_2^{scope2}– emissions (Scope 2), kt CO_2-eq/y.	–

the in-house model (for further information see (Tan et al., 2024)). For estimating water consumption, it was assumed that the water was disposed of after waste treatment. Within the boundaries considered, biomass was assumed to be CO_2-neutral, and emissions from transporting the biomass were not considered.

2.3.2. *Sensitivity analysis*

A sensitivity analysis was conducted to explore the potential impacts of fluctuations in biomass, electricity, and steam prices on the minimum selling price (MSP) and OPEX of bio-isobutene. The range of variation of the prices was assumed to be ±75 % above and below the market price (year 2018).

2.4. *Impact assessment on the current structure of the cluster*

To identify potential impacts at the cluster level, a graphical network representation of the process units (i.e., blocks) and the connections between them (i.e., mass and energy flows in the form of links) was developed for the two cases, fossil-based and with the ACS-based isobutene. Then, to identify the main changes, both networks were compared. The changes in the flows were categorised as (i) removed (i.e., 100 %), (ii) affected (i.e., the flow is reduced/increased), (iii) unchanged, or (iv) added (i.e., 100 % new flow). In the second step, the impact of the structural changes was evaluated using the TEE indicators shown in Table 1 (see Section 3.2).

3. Results and discussion

3.1. *Performance assessment of ACS- vs fossil-based isobutene processes*

3.1.1. *Comparison of mass and energy balances*

The mass balances and net energy requirements of the fossil- and bio-IBN processes are presented in Fig. 3 and Table 2. The models are validated by comparing ratios of auxiliary chemicals used (e.g., solvents) to the amount of biomass consumed in data reported in the literature (see Table 8). As shown in Fig. 3, a key difference between the fossil- and bio-IBN processes is the change in the use and production of chemicals. The fossil-based process produces only isobutene, while the ACS-based process has CO_2, n-Butenes and furfural as by-products.

Table 2
Net energy requirements, cooling needs and economic performances of fossil- and ACS-based isobutene production processes. A negative value represents the extra production of the power/energy. LLPS – very low-pressure steam; LPS – low-pressure steam; MPS – medium-pressure steam; HPS – high-pressure steam.

		Fossil-based case	ACS-based case	ACS-based case with VC-HP
LLPS	PJ/y	–	120	−7.8
LPS	PJ/y	–	−1.6	−1.6
MPS	PJ/y	0.6	5.4	5.4
HPS	PJ/y	–	−1	−1
Cooling water	PJ/y	0.5	160	120
Electricity	PJ/y	0.04	0.3	29
CAPEX	MEUR	16	1171	2430
OPEX	MEUR/y	665	3568	1366

The findings also show that using the bio-based route would significantly increase heat and cooling requirements (see ACS-based case under Table 2). However, part of the heat needs in the bio-based process is covered by an internal heat generation unit (HGU) (the unit burns bio-waste streams from the bio-isobutene production), while in the case of the fossil-based process, all utilities are bought from the market. The heat generated by HGU from bio-IBN covered 25 % of the medium-pressure steam (MPS) required in the bio-IBN process (i.e., it fully covers both the organosolv and isobutene production stages), but only 14 % of the total process needs of very low-pressure steam (LLPS). The major contributors to the energy requirements from the bio-IBN process are the columns from the recovery and distillation units of ethanol-water separation, accounting for up to 87 % of the total energy needs of the process. This is mainly due to the need to separate highly diluted products formed after the organosolv reactor (Bulkan et al., 2021) (43 %(wt.) water and 41 %(wt.) ethanol (solvent), see Appendix A, SI file, Table S.5). All columns operate at low temperatures of 78–98 °C (note that the boiling point of ethanol at 1 bar is 78.4 °C, of water is 100 °C,

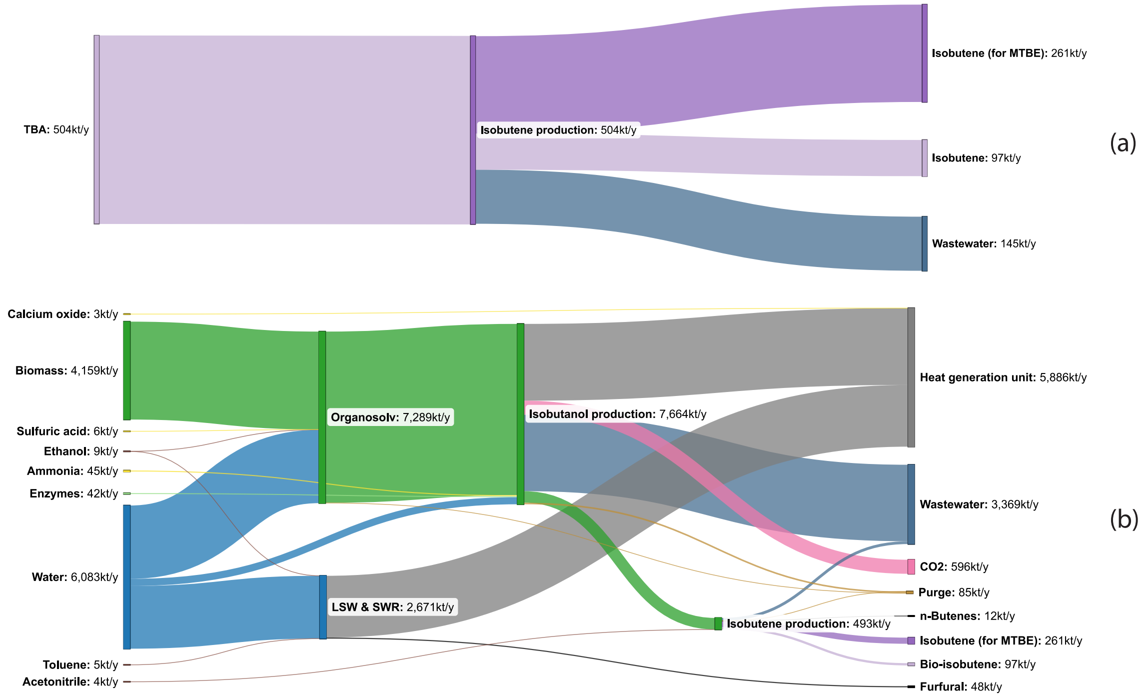


Fig. 3. Mass flows of (a) fossil-and (b) bio-IBN isobutene production processes. LSW & SWR - lignin and solvent wash unit and solvent and water recovery unit.

and of the azeotrope is 78.3 °C), which results in considerable LLPS and cooling water. Using a VC-HP could reduce up to 91 % (128 PJ/y) and 29 % of the total LLPS and cooling water consumption, respectively (see ACS-based case with VC-HP in Table 2), but required almost 27 PJ/y of more electricity. The CAPEX of the ACS-based case using a VC-HP is 2 times higher compared to the case without heat pumps, while the OPEX is reduced by 62 %. The share of the annualised CAPEX of the VC-HP is 188 MEUR/y, while annual savings due to the reduction in OPEX are in the order of 2200 MEUR.

In comparison, the bio-IBN process using VC-HP has an excess of high-pressure steam (HPS), LPS and LLPS, while all three are neither produced nor required in the fossil-based process. However, the ACS case results in a significant increase in MPS (9 times) and cooling water consumption (240 times), followed by the additional electricity required for the compressor work of the HPs. The differences in energy profiles between the two processes emphasise the importance of evaluating the potential of heat and mass integration of new processes into existing clusters.

3.1.2. *Techno-economic performance assessment*

Table 3 provides an overview of the TEE indicators for both cases, which are discussed in the following sections. As the bio-IBN case produces several by-products, the values of the indicators for the case are presented both as absolute and allocated to the 358 kt/y of isobutene produced.

The results show a significant decrease in fossil feedstocks in the process as a consequence of implementing the ACS-based route, from 504 kt/y to 18 kt/y (see Fig. 3). In the fossil process, 100 % of the carbon entering the process comes from the TBA stream. In the bio-IBN, 1966 kt/y of carbon comes from biomass, accounting for 99 % of the total carbon entering the process (see Table 3), from which 10 % of carbon is embedded in the byproducts and 74 % in the waste streams. The results show that the higher complexity of the ACS-based process compared to the relatively simple fossil-based process results in significantly higher bare equipment costs and, thus, higher CAPEX (see Table 3). The high bare equipment costs of the bio-IBN process are primarily due to the higher number of equipment used. The bio-IBN process requires 4 Mt/y of biomass, yet the market price of the latter one is 13 times lower than the TBA price, resulting in 2 times lower raw materials costs compared to the fossil-based process. Still, the OPEX of the bio-based case is significantly higher than the fossil-based one (2 times) due to higher cooling water and electricity requirements. As a result, the annual operating cost of the ACS-based process is 2 times higher than that of the fossil-based one.

Table 3
Techno-economic and environmental indicators for the performance assessment (based on Table 1).

Indicator			Fossil-based case	ACS-based case	
	Abbr	Units	Absolute	Absolute	Allocated
Techno-economic					
Carbon feedstock	C_f	kt/y	318	1977	1226
Total steam consumption	TEC_{steam}	PJ/y	0.6	−5	−3.1
Total cooling water consumption	TEC_{CW}	PJ/y	0.5	120	74
Total electricity consumption	$TEC_{electricity}$	PJ/y	0.04	29	18
Capital expenditures	CAPEX	MEUR	16	2430	1507
Operational expenditures	OPEX	MEUR/y	665	1366	847
Equivalent annual operating costs	EAOC	MEUR/y	667	1593	988
Minimum selling price	MSP	EUR/tonne	1503	3776	–
Environmental					
Total water consumption	TWC	kt/y	97	39,441	24,453
Total bare land requirement	TL	m^2	46	4145	2570
Total CO_2 emissions	CO_2^{total}	kt CO_2-eq/y	122	8424[a]	5223

[a] 42 % are from biogenic origin (see Section 3.1.3, Table 4).

Table 4
Total CO_2 emissions of fossil- and ACS-based isobutene production processes (i.e., Scope 1 and Scope 2, based on Table 1). WFB – waste-fired boilers; CHP – combined heat and power plants; HGU –heat generation unit.

	Fossil-based case		ACS-based case	
Scope 1: Process-related CO_2 emissions				
	CO_2, kt/y	Origin	CO_2, kt/y	Origin
From the production process	–	–	28	biogenic
From internal HGU/CHP/WFB	–	–	3534	biogenic
Sub-total CO_2 emissions	–	–	**3562**	biogenic
Scope 2: Energy-related CO_2 emissions				
From utilities	CO_2, kt/y	Origin	CO_2, kt/y	Origin
LLPS	–	–	–	–
LPS	–	–	–	–
MPS	117	non-biogenic	1029	non-biogenic
HPS	–	–	–	–
Electricity	5	non-biogenic	3833	non-biogenic
Sub-total CO_2 emissions	**122**	non-biogenic	**4862**	non-biogenic
Total CO_2 emissions	**122**	non-biogenic	**4862**	non-biogenic

The higher CAPEX and OPEX results on the MSP of the bio-IBN being 2.5 times higher than the fossil case and 2.3 times higher than the market price. Note that in this assessment, it was assumed that the LLPS, LPS and HPS that are not used in the process (i.e., excess) are sold to the market, and as a result, 25 % of the revenue of the bio-IBN is from selling steam. If this is not possible, the MSP of the ACS case would be 2.7 times higher than the market price.

3.1.3. *Environmental performance*

Table 4 summarises the CO_2 emissions from both production processes. The results show that the fossil-based process has no Scope 1 emissions as the process does not generate any waste streams. In the bio-IBN case, biomass residues (i.e., lignin, pulp and solid fractions) are used for in-situ steam production, and therefore, all Scope 1 emissions of the ACS-based case are of biogenic origin. However, when Scope 2 emissions are considered, the picture changes as the bio-based case also requires a high amount of additional electricity and heat from the market (see Section 3.1.1). In this paper, it was assumed that the market uses natural gas as feedstock to produce utilities (reflecting the current situation), and Scope 2 emissions of the ACS case are c.a. 40 times higher than those of the fossil base case. If renewable sources were used instead, the impacts could be significantly lower. This highlights the importance of decarbonising heat and electricity when implementing ACS-based processes.

The ACS-based case has considerable water consumption (see Fig. 3 or Table 3) due to the organosolv and solvent wash sections accounting for 46 % and 49 % of the water consumed. Consequently, the ACS-based process generates 46 times more wastewater compared to the fossil-based case (see Appendix A, SI file, Table S.7). Although a higher amount of wastewater is sent back to the water source after water treatment compared to the fossil-based process, the total water consumption for producing 358 kt/y of isobutene in the ACS-based process is 252 times higher, mostly due to the losses associated with the higher utility usage (i.e., cooling water).

Finally, one aspect that is often ignored when conducting technology assessments of ACS processes is land requirements. The difference in total bare land requirements between the fossil-based and bio-IBN processes is 90 times, which reemphasises the need to evaluate the special constraints of integrating a new process into existing clusters.

3.1.4. *Sensitivity analysis*

Fig. 4 presents the results of the sensitivity analysis. It shows that changes in electricity prices have a higher effect on the MSP than biomass and steam price fluctuations. Changes in electricity prices affect the MSP of isobutene by 50 %, while similar changes in biomass and steam prices only affect the MSP by about 12 and 7 %, respectively. This is because 80 % of the MSP comes from the OPEX, of which 67 % comes from the costs of utilities and 21 % from the raw materials. Increasing the steam price lowers the bio-isobutene MSP due to excess steam production, but the fluctuation is minor (7 %). Even with the lowest prices of raw materials or utilities, the MSP of isobutene is still far from its market price and remains between 1.2 and 3.4 times higher.

3.2. *Impact assessment at cluster level*

Besides examining the performance at the process level, this work additionally explores the implications at the cluster level after deploying the ACS-based process. The mass balances and net energy requirements of the fossil and bio-MTBE clusters are presented in Fig. 5 and Table 5. Fig. 6 shows the main changes in material and energy flows and units of the existing processes in the MTBE cluster (fossil-based) if the bio-IBN process would be deployed in the cluster.

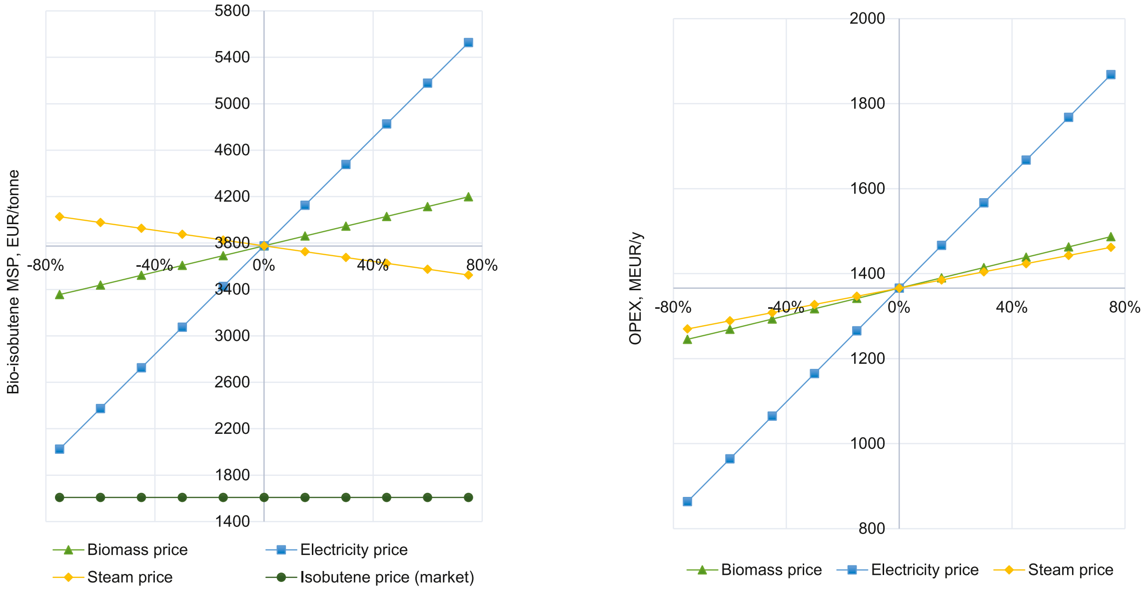
Two changes in the structure of the cluster need to be highlighted (see Fig. 6). The first is that the bio-IBN production process does not require TBA (504 kt/y). However, in the PoR, TBA is a byproduct of a process that produces PO and TBA (where PO is the main product); therefore, as far as PO is produced, TBA will still be produced in the cluster regardless of its further use. It could be considered for sale to the market. However, as this is fossil TBA, it remains questionable whether this will be possible in the future (if there is no market for fossil-based chemicals). Second, as the purpose of the fossil-based isobutene production (and related flows) is to provide a raw material for MTBE production, which is now substituted by isobutene produced from the bio-IBN process, thus the isobutene production process (fossil-based) is not needed in the ACS-based cluster. Note that due to the production of PO, upstream units, and therefore their material and energy requirements, remain unchanged.

Fig. 5 shows that the deployment of the bio-IBN process affects the overall amount of feedstocks consumed in the cluster, which is now 2.6 times higher than the base case. The feedstock profiles differ in the ACS-based cluster, with around 36 % of the feedstocks being from bio-based sources, 26 % from fossil-based origin, and 46 % from process water.

For the energy needs of the fossil-based cluster, the waste-fired boilers, which currently burn waste-fuel streams from two processes in the cluster (C4 isomerisation and PO/TBA production), cover about 93 % of the total demand of LLPS required for PO/TBA process (see Appendix A, SI file, Table S.6). Of the remaining 7 %, around 6 % is supplied from the MTBE process, and the rest is bought from CHPs in the cluster and/or market. The remaining power and energy needs of the processes in the fossil-based MTBE cluster are covered by the existing CHPs in the cluster or bought directly from the market (see (Tan et al., 2024) and Appendix A, SI file, Table S6).

Because of deploying the new bio-IBN process, there is a shift in energy consumption (see Table 5). There is also a significant increase in cooling water and electricity after integration, 4.2 and 3.4 times, respectively. Notably, the generated LLPS and LPS steam from the ACS-based process can fully or partially cover the needs of the fossil-based cluster. However, additional MPS, cooling water and electricity are still required to cover all the needs of the integrated bio-IBN process. Furthermore, although the energy flows that were originally supplied to the isobutene process (fossil-based) can be utilised for the ACS-based process, they only cover about 11 % of the MPS and less than 0.1 % of the electricity and cooling water required by the bio-IBN process.

It is also worth noting that the CAPEX of the added bio-IBN process is almost an order of magnitude higher than the total CAPEX of the fossil-



(a)   (b)

Fig. 4. Results from the sensitivity analysis: (a) changes in the MSP of bio-isobutene; (b) changes in OPEX of the bio-IBN process.

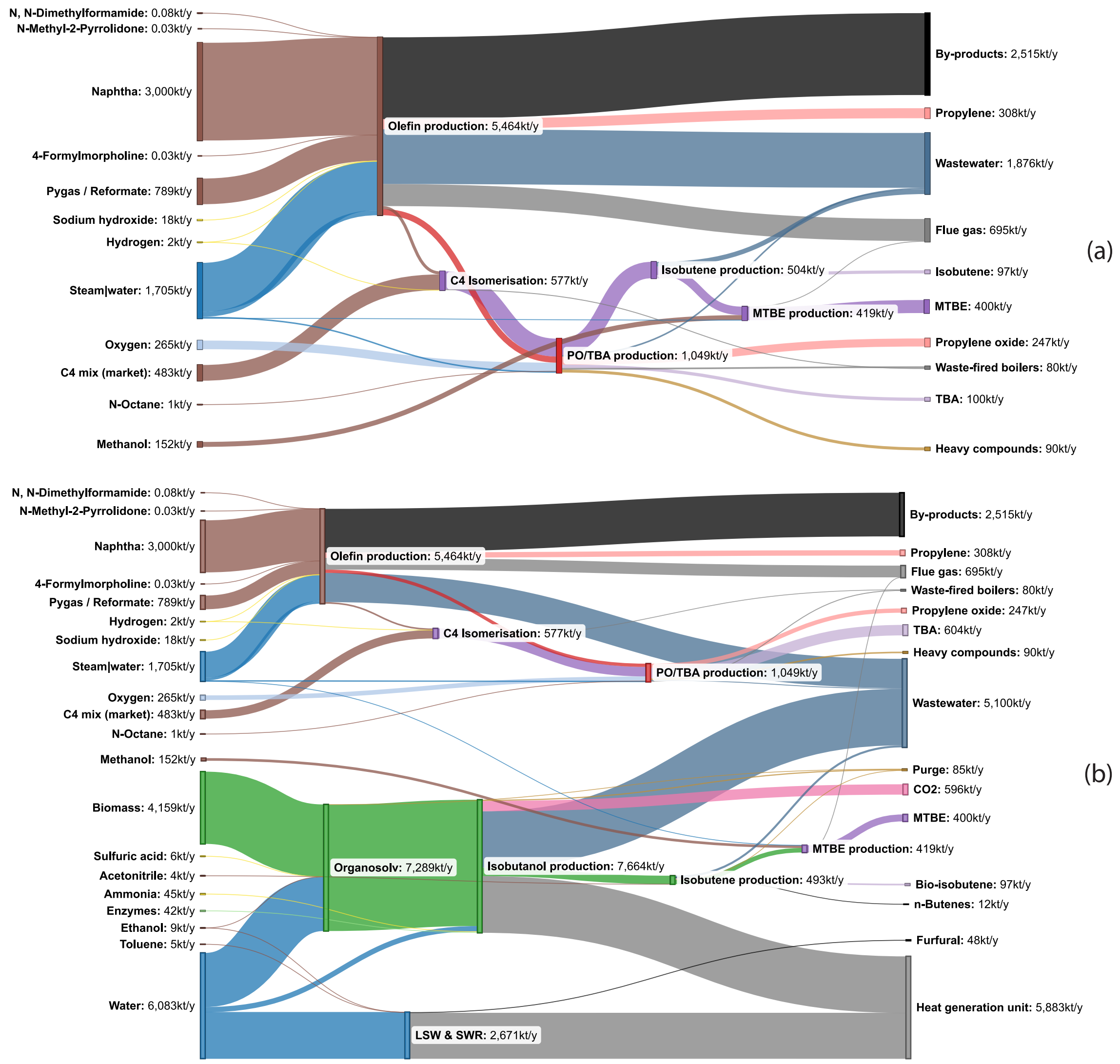


Fig. 5. Sankey diagram of mass flows of (a) fossil- and (b) ACS-based MTBE cluster. LSW & SWR - lignin and solvent wash unit and solvent and water recovery unit.

Table 5
Net energy requirements and cooling needs for both clusters (for more details regarding fossil-based MTBE cluster, please see Table 8 and Appendix A, SI file, Table S.6). A negative value represents the extra production of the power/energy. LLPS – very low-pressure steam; LPS – low-pressure steam; MPS – medium-pressure steam; HPS – high-pressure steam.

Cluster	Utility type	LLPS	LPS	MPS	HPS	Cooling water	Electricity
Fossil-based	PJ/y	2	6.6	−2.3	−5.6	36.6	12
ACS-based	PJ/y	−5.8	5	3.1	−6.6	157	41

based MTBE cluster (see Table 6). The OPEX associated with the ACS-based case increases the total OPEX of the cluster by 61 %. Savings from the wastewater treatment after the fossil-based isobutene production are about 0.22 MEUR/y.

As for the environmental performance of the MTBE cluster (see Table 6), the total water consumption of the bio-IBN process is 1.5 times higher compared to the TWC of the MTBE cluster (fossil-based). Thus, deploying the bio-IBN process would result in 3 times higher TWC of the ACS-based cluster than the fossil-based one.

Comparable to the bio-IBN process, the major share of the CO_2 emissions from the processes in the fossil-based cluster comes from the Scope 2 emissions. The bio-IBN process, which requires a high amount of steam and electricity (still produced from fossil-based sources; see Sections 3.1.1 and 3.1.3), significantly increases (2 times) CO_2 emissions of the defossilised cluster, which again underscores the critical importance of decarbonising heat and electricity.

Finally, Table 7 shows the land footprint of the different processes. It appears that 42 % of the equipment in the bio-IBN process are columns with a large footprint. The number of columns used and the total land footprint of the ACS-based case result in the same order of magnitude as existing refineries (José, 2017). Thus, deploying the bio-IBN process would 2 times enlarge the bare land requirement of the existing MTBE cluster and would require a significant amount of land in the PoR. Note that the values in Table 7 are only for bare equipment, and therefore, the real footprints will be larger as they do not include land requirements for control equipment, pipelines, storage, utilities and others.

3.3. Implications and limitations

The study emphasises the need to look beyond one-to-one comparison of the processes inside existing petrochemical clusters during ex-ante analysis and assess their deployment, applicability, and impact. The study proposes performance assessments for the process and cluster levels, which could be used as an example for the defossilisation of other

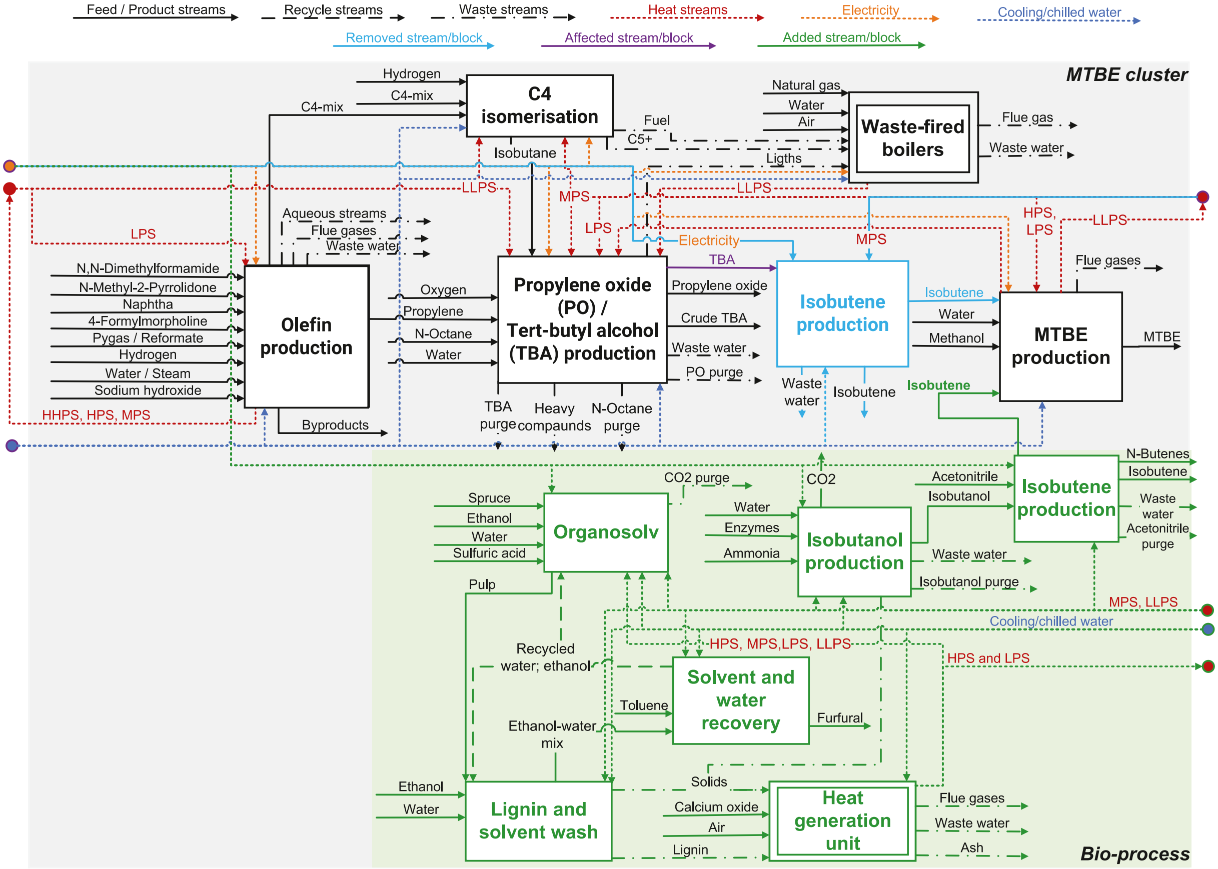


Fig. 6. Changes at the cluster level due to bio-IBN production as part of the MTBE cluster. The figure shows the units/streams that would disappear (in blue) and stay but are affected (in purple) and the new units and flows (in green).

Table 6
Changes in the economic and environmental performances of the cluster (based on Table 1).

Process	Structural changes	Economic		Environmental	
		CAPEX	OPEX	TWC	CO_2^{total}
		MEUR	MEUR/y	kt/y	kt $CO_{2\text{-}eq}$/y
Olefin production	unchanged	1130	2900	7943	3884
C4 isomerisation	unchanged	37.3	309	1057	406
PO/TBA production	unchanged	129	107	3105	416
Isobutene production	**removed**	**−16**	**−22**	**−97**	**−122**
Waste-fired boiler	unchanged	139	36	1671	314
MTBE production	unchanged	26	173	5370	510
Bio-IBN production	**added**	**2430**	**1366**	**39,441**	**4862**

processes. The findings of the work would be valuable for decision-makers from industry and policy involved in designing sustainable strategies. Additionally, the work provides well-documented model data (see Table 8), allowing future researchers to replicate models by reusing assumptions for the proposed design.

While the work provides important insights, it has limitations associated with the scope and assumptions. Firstly, this work focuses on deploying one bio-IBN production route (i.e., organosolv, hydrolysis, dehydration), leaving out other potential options (e.g., dilute-acid pretreatment, fermentation). Thus, to draw complete conclusions about which route is the most optimal for the IBN production in the existing (fossil-based) cluster, assessing and comparing the performance of the other ACS-based routes before and after their deployment is crucial. Additionally, the modelling results point out further work required to improve the bio-IBN model, mainly optimisation of the heat integration. The gate-to-gate boundary should be expanded for a complete environmental life cycle assessment. Moreover, land availability is required to be considered while assessing the transition of the petrochemical cluster, as the latter ones are usually within populated areas, with limited land for new processes to be integrated. Lastly, the study focuses on the assessment of deploying one single alternative process, while in real-world scenarios, possibly two or more DD processes can be defossilised simultaneously.

4. Conclusions

This research stresses the need and importance of looking beyond one-to-one comparison in ex-ante analyses of the new processes and further developing the understanding of the impacts after deploying them in existing industrial clusters. To support that, a case study is used to illustrate the deployment of the bio-IBN process in place of the fossil-based one in the existing MTBE production in the Port of Rotterdam. While the performance at the process and cluster levels was evaluated using proposed techno-economic and environmental KPIs, the structural changes at the cluster level were identified using impact assessment. At the process level, biomass usage for bio-IBN production shifts the carbon source from fossil-based to 99 % biogenic. However, the bio-IBN process (on an industrial scale) is currently not competitive with the fossil-based one. This is mainly due to the high complexity of the process, which results in higher bare equipment costs and utility usage (caused mainly by the distillation units after the organosolv reactor) and affects the CAPEX and OPEX. The CO_2 emissions (Scope 1 and 2) of the bio-IBN are highly affected by the carbon footprint of the steam and electricity used

Table 7
Number of equipment and bare land required for the fossil-based MTBE cluster and bio-IBN process (based on the Aspen Plus APEA, see Table 8). T_e - Total number of equipment; C - Columns; TL – Total land requirement; E_c - Bare equipment costs.

Fossil-based cluster					Bio-IBN process				
Process	T_e	C	TL, m^2	E_c, MEUR	Process	T_e	C	TL, m^2	E_c, MEUR
Olefin production	118	24	1316	177	Organosolv pretreatment	23	–	127	14
C4 Isomerisation	19	3	181	7	Lignin and solvent wash	23	2	395	23
PO/TBA production	60	11	542	26	Solvent and water recovery	85	67	2232	734
Isobutene production	11	1	46	3	Isobutanol production	19	3	191	19
Waste-fired boilers	14	–	112	28	Isobutene production	19	4	176	11
MTBE production	17	3	70	5	Heat generation unit	14	–	1026	18
Total:	**239**	**42**	**2267**	**247**	**Total:**	**183**	**76**	**4145**	**819**

Table 8
Detailed process data sheets of the models used in the performance assessment.

Process	Feedstock type	DOI
Olefin production	Fossil-based	https://doi.org/10.5281/zenodo.14825234
C4 isomerisation	Fossil-based	https://doi.org/10.5281/zenodo.14825844
PO/TBA production	Fossil-based	
Isobutene production	Fossil-based	https://doi.org/10.5281/zenodo.14825922
MTBE production	Fossil-based	
Waste-fired boiler	Fossil-based	https://doi.org/10.5281/zenodo.14825977
Bio-IBN production	ACS-based	https://doi.org/10.5281/zenodo.14826089

from the market. If steam and electricity are produced from fossil sources (as is today the case), the ACS-based case would result in significantly higher CO_2 emissions than the fossil-based case. This stresses the need for additional improvements in the process layout to enhance bio-IBN process competitiveness and include externality costs in the fossil-based process.

At the cluster level, the deployment of the bio-IBN process changed the existing structure of MTBE production, as the isobutene process (fossil-based) would no longer be required. As a result, there is a shift in energy requirements of the MTBE cluster, primarily enlarging its MPS and electricity needs (still produced from fossil-based sources), resulting in (2 times) higher CO_2 emissions (Scope 2). This highlights the necessity of decarbonising heat and electricity sources while defossilising the MTBE cluster in the PoR. Furthermore, the results have shown that bio-IBN requires 90 times more bare land than the fossil-based process. Thus, defossilisation of the MTBE cluster in the PoR by integrating the bio-IBN process would significantly enlarge the required land footprint of the full cluster by a factor of 2. This highlights the importance of examining land requirements, often overlooked in ex-ante assessments. In the present work, bio-IBN production would require about 4 Mt/y of biomass to reach the same amount of the fossil-based isobutene produced inside the MTBE cluster today. Thus, finally, an aspect that needs further research regards the availability of non-fossil feedstocks and the implications for their use in the chemical industry.

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CRediT authorship contribution statement

Inna Stepchuk: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Formal analysis, Data curation, Conceptualization. **Mar Pérez-Fortes:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Andrea Ramírez:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2025.145114.

Data availability

The data is provided in the supplementary information (SI) file and Table 8 (DOI links).

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