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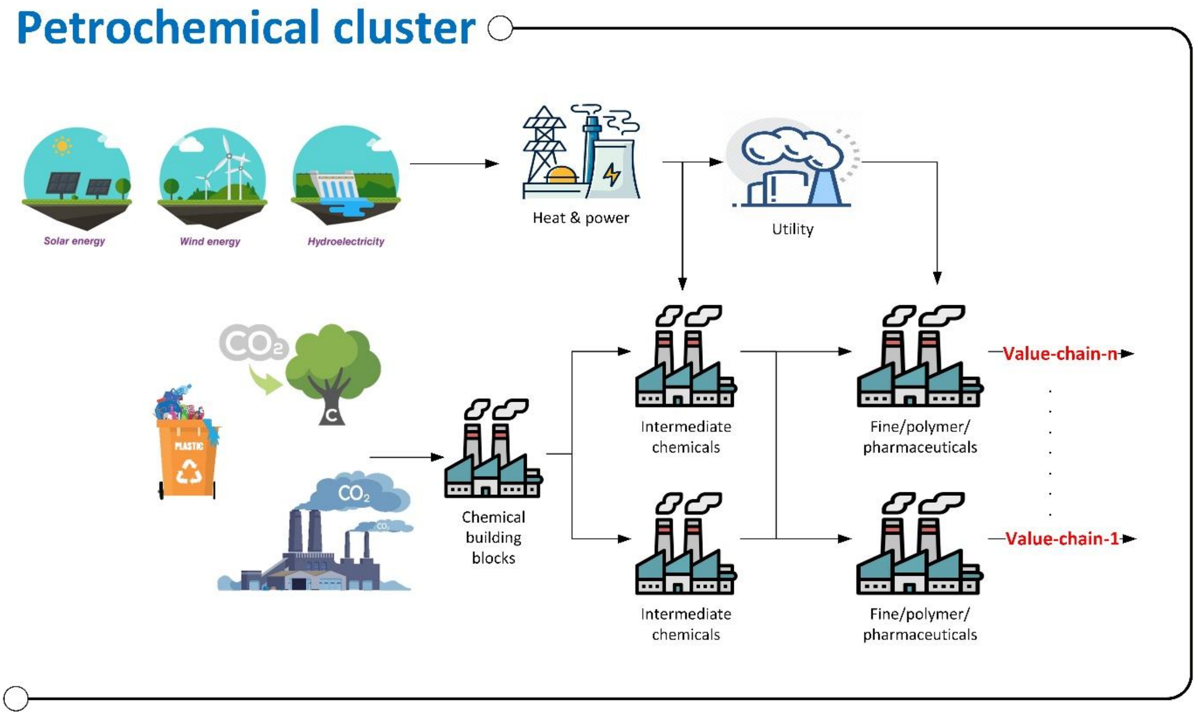

James Tonny MANALAL

Reimagining petrochemical clusters by defossilising chemical building blocks

Dissertation

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Contents

Summary

Today's day-to-day essentials like packaging, cosmetics, medicines, fertilisers, detergents, paints and fuels are made primarily from fossil-based raw materials such as crude oil or natural gas. To reach the ambitious CO_2 emission reduction targets needed to mitigate climate change, replacing the use of fossil-based feedstocks with sustainable carbon feedstocks (i.e. defossilisation) will be vital. In today's petrochemical industry, fossil-based raw materials are first broken down into chemical building blocks (CBB) such as carbon monoxide, methanol, ethylene, propylene, benzene and xylene before further processing into intermediate chemicals and the day-to-day essentials. These CBB are the backbone of the chemical sector.

CBB production can be defossilised by using alternative carbon sources (ACS) such as CO_2, biomass and plastic waste as feedstocks. However, changing the feedstock to produce CBB is not just limited to changing a given technology, as CBB are generally produced in highly interconnected petrochemical clusters. Petrochemical clusters are a spatial concentration of related and/or directly connected industries. They provide competitive advantages in terms of shared infrastructure, knowledge, materials, and or energy. Thus, changes in feedstock can result in ripple effects along the interconnected value chains. Identifying and quantifying such ripple effects at process and cluster levels were the focus of this dissertation.

The overarching aim of this PhD thesis was to understand **the impacts of defossilising the production of chemical building blocks in existing petrochemical clusters**. To answer this question, three sub-research questions were proposed, as shown below.

How can the use of alternative carbon sources (ACS) affect the production of chemical building blocks in existing petrochemical clusters?	
Sub-research questions (SRQ)	*SRQ-1: How to screen promising ACS-based process routes at different TRLs to produce chemical building blocks?*
	SRQ-2: What are the techno-economic impacts of using ACS-based technologies for the production of chemical building blocks in existing petrochemical clusters?
	SRQ-3: How does the availability of alternative carbon sources affect potential technology portfolios for defossilising the production of chemical building blocks in existing petrochemical clusters?

The reference and ACS-based technologies were modelled in Aspen Plus with design, operating capacities and process complexities similar to those in current CBB production plants in the Port of Rotterdam (PoR), the Netherlands. The technologies were then assessed using key performance indicators (KPIs) at both process and cluster levels. Finally, this thesis evaluated the technology portfolio required for defossilising the production of CBB (methanol, ethylene, propylene, benzene, p-xylene) and examined how limitations in ACS feedstock availability could affect the design and performance of a defossilised brownfield petrochemical cluster. The highlights of the key findings of the research are as follows:

Screening promising ACS-based process routes at different TRLs for the production of chemical building blocks

With the need to defossilise the petrochemical sector, many possible process routes that use ACS are under development. For instance, more than 65 different ACS-based process routes were identified in the literature for producing ethylene. These multiple options are at different technology readiness levels, making the selection of promising process route a complex task.

A screening methodology based on the stage-gate concept was developed to select promising ACS technologies to further study in this thesis. The method used ideal stoichiometric reactions and thermodynamic state functions at standard temperature and pressure conditions with carbon utilisation efficiency, electricity and heat needs as key performance indicators.

The assessment showed that the C:H:O ratio of the ACS feedstocks played a major role in the technical performance of the process as higher oxygen content in the feedstock results in lower carbon utilisation efficiencies or higher hydrogen need. For example, given that the oxygen content of CO_2, biomass and plastic waste are 73 wt%, 49 wt% and 0 wt% respectively; CO_2 requires the highest energy input for oxygen removal through hydrogenation or electrochemical reduction for CBB production. Plastic waste, which has a similar C:H:O composition compared to the fossil fuel-based feedstocks, scored better than biomass and CO_2 based technologies in the screening methodology.

The results also showed that assumptions regarding the origin of hydrogen significantly impact the ranking of technologies. For example, when assuming that hydrogen is imported, the screening methodology identifies exothermic technologies based on hydrogenation of CO_2-to-methanol and oxygen gasification of biomass or plastic waste as preferable routes for further examination. If, however, the production of hydrogen is done onsite, direct electrochemical reduction, biomass steam gasification and plastic waste pyrolysis are ranked higher than the exothermic routes mentioned above, in terms of material and energy efficiencies. This is because the material and energy penalties of the highly endergonic hydrogen production processes were not included in the hydrogen import case.

This research highlights how a relatively simple stoichiometry based stage-gate method can be used for technology screening and how assumptions on hydrogen origin can significantly change R&D portfolios.

Techno-economic impacts of using ACS-based technologies for the production of chemical building blocks in existing petrochemical clusters

Replacing fossil-based processes in interconnected industrial clusters can impact upstream supply chains, downstream units, energy islands, waste treatment plants, and change the overall performance of a cluster. This, however, has been overlooked in the literature. To address this knowledge gap, the impact of the ACS-based production routes (selected using the screening methodology) were analysed at cluster level by assessing changes in mass, energy, prices, CO_2 emissions and water demand. The results show that due to the significant differences in product distribution, energy needs, and waste generation of ACS-based processes, the petrochemical cluster will need to undergo significant reconfiguration efforts both in terms of mass and energy flows.

At the process level, the main challenges to defossilisation olefins and aromatics were (i) access to large quantities of renewable electricity at cheap prices, particularly for hydrogen production, and (ii) the large investment costs of ACS-based processes compared to fossil fuel-based technologies. In general, plastic waste-based technologies showed a better performance than the biomass and CO_2 based technologies, due to their better C/H ratio of the feedstock, leading to lower external hydrogen demand and higher product yields.

For olefins, at the cluster level, replacing the naphtha cracker with ACS-based technologies poses significant challenges. This is mainly due to differences in product profiles and the need for substantial changes in electricity, water, and waste treatment infrastructure. On average, the ACS-based processes studied in this thesis needed 5 to 10 times more electricity and water per unit of ethylene produced. The significant difference in utility needs would require a complete overhaul of the energy and utility plants to integrate the ACS-based processes into the cluster. Ripple effects on the structure of the cluster due to defossilisation were seen because of the difference in the product-to-byproduct ratio (i.e., mainly for propylene, offgases and heavy hydrocarbons in the ACS cases. This was particularly the case for the CO_2-based direct electrochemical reduction process to produce ethylene, in which no propylene is produced. As a result, propylene would need to be imported, introducing logistical and environmental challenges if for instance, the propylene would be of fossil origin .

For aromatics production, among the ACS-based routes, the plastic waste-based methanol-to-aromatics route was the most competitive, with the lowest impact at the cluster level. At the cluster level, the main differences among the processes were found in the production of xylene, off gas production, electricity and water requirements, and waste treatment infrastructure. Significant differences in utility needs were mainly due to the high hydrogen need and higher pressure requirements for the methanol production process compared to the existing fossil-based processes. The higher water demand was due to the water electrolysis and steam gasification process required to produce the syngas needed for the methanol production process. About 80%-90% of both the electricity and CAPEX was accounted by the ACS to methanol production process. Thus, for the ACS-based aromatics process, the techno-economic performance of the methanol production process played both a key role at the process and cluster level.

Integrating ACS-based technologies resulted in lower fossil carbon content and significant price changes along the value chains. For example, a +134% price change in the levelised cost of ethylene from an ACS processes would alone result on a 97% increase in price of polyvinyl chloride and a 34% price increase in polyethylene terephthalate. The varying price impacts along the value chain are due to differences in CBB needed in the production processes, reference prices and process yields. Among the different olefin and aromatic value chains, polyvinyl chloride, acetone, cyclohexane and polyethylene terephthalate appeared as the most impacted both in terms of reaching the highest defossilisation and highest price impacts. This is because on those value chains, 80% to 100% of the embedded carbon originates from olefins and aromatics, respectively. Compared to the defossilisation of olefins, defossilising aromatics resulted on the highest change in embedded carbon in the cluster, as aromatics account for over 50% of the embedded carbon in the cluster.

For both ACS-based olefins and aromatics processes, the large electricity need, hydrogen consumption, and waste generation resulted in other impacts such as higher water consumption, wastewater generation, and CO_2 emissions, which, if not addressed properly, could nullify the purpose of defossilising chemical building blocks. The analysis shows that further improvements in waste valorisation and the integration of renewable energy will be required to ensure the climate change benefit of ACS-based technologies. ACS-based technologies should therefore be deployed in tandem with renewable energy-based utilities and wastewater recycling plants for the system to be low-carbon and reduce water stress.

Impact of availability of alternative carbon sources on the potential technology portfolios for defossilising the production of chemical building blocks in existing petrochemical clusters

For producing the same quantity of CBB, larger quantities of ACS-based feedstocks will be required compared to fossil-based feedstocks due to the low carbon and hydrogen content of ACS-based feedstocks. The availability of ACS will not only affect the limit up to which a petrochemical cluster can be defossilised, but also the technology portfolio required for CBB production. In this study, the technology portfolio required for defossilising a brownfield petrochemical cluster were analysed considering two objective functions (i) minimising fossil carbon use and (ii) minimisation of CAPEX penalty (defined as the sum of new investment plus the loss CAPEX due to removing existing assets) to limit the change in existing infrastructure. Three cases were explored: a reference case, and two cases defined by availability of ACS feedstocks. One with no limits and another with limited availability.

A comparison of the technology portfolios between the unlimited and limited ACS cases showed a variation of 2 to 8 times in CAPEX penalty, energy estimates and water demand. Achieving a 95% defossilisation rate resulted in a significant capital expenditure (CAPEX) penalty of approximately €33 billion, alongside an electricity demand of 65 PJ per year. This contrasts sharply with the reference case, which required only €2 billion in CAPEX and 7 PJ per year of electricity. Furthermore, water demand in the cluster rose from 2 million tonnes per year in the reference case to 14 million tonnes per year in the defossilisation scenario with unlimited availability of feedstocks, primarily driven by the steam gasification process used to convert plastic waste into methanol via syngas To achieve up to 95% defossilisation for the production of chemical building blocks, about 19.5 Mt/y plastic waste would be required, which is over three times higher than the current plastic production in the Netherlands. When sufficient plastic waste would be available, among the plastic waste-based ACS technologies, the methanol-based process was selected, as methanol could be converted to both olefins and aromatics.

When limitations in feedstocks were included in the model, the maximum defossilisation obtained was 55% of CBB production. This case required around 200 PJ/y electricity, 3 Mt/y of CO_2, 8 Mt/y biomass and 7 Mt/y of plastic waste. Olefin production was partially defossilised using synthetic naphtha from plastic waste-based pyrolysis, aromatics production was defossilised using a methanol to aromatics process, and hydrogen production was defossilised using water electrolysis. The study estimated that around 35 billion EUR of CAPEX penalty will be incurred to defossilise up to 55% of the cluster, which is about 18 times the CAPEX of the fossil-based CBB production plants in the model due to the need to deploy more expensive technologies. The water demand in the cluster increased from 2 Mt/y in the reference case to 8 Mt/y, mainly due to the steam gasification process required for converting plastic waste and biomass to methanol via syngas and hydrogenation of CO_2-to-methanol. The results indicate that, given ACS feedstock limitations and current demands of CBB, a combination of ACS and fossil-based technologies will need to co-exist. There is no single “silver bullet” process or feedstock that can fully defossilise CBB production; instead, a combination of ACS feedstocks will be required.

This work points out that ACS feedstock limitations will significantly impact the performance of existing brown-field industrial clusters. The magnitude of energy and material required for such a change shows that a large challenge for existing petrochemical clusters, similar to the Port of Rotterdam, will be the 5 to 10 times higher electricity and water needs. This shows that either the production capacities of chemical processes need to be downscaled or strategic decisions regarding which chemical to produce in the cluster have to be made. Another option is to import intermediate renewable carbon feedstocks like methanol, pyrolysis oil, ethanol or Fischer Tropsch naphtha into the cluster. However, as these processes are highly energy, CAPEX, and land-intensive processes, this shift may result in increasing environmental impacts outside the Netherlands, which will need to be examined.

Samenvatting

Producten voor dagelijks gebruik zoals verpakkingen, cosmetica, medicijnen, meststoffen, wasmiddelen, verf en brandstoffen, worden voornamelijk gemaakt van fossiele grondstoffen zoals ruwe olie of aardgas. Om de ambitieuze doelstellingen voor CO_2-emissiereductie te halen die nodig zijn om klimaatverandering tegen te gaan, is het essentieel om het gebruik van fossiele grondstoffen te vervangen door duurzame koolstofgrondstoffen (d.w.z. defossilisatie). In de huidige petrochemische industrie worden fossiele grondstoffen eerst afgebroken tot chemische bouwstenen (CBB) zoals koolmonoxide, methanol, ethyleen, propyleen, benzeen en xyleen, alvorens ze verder worden verwerkt tot intermediaire chemicaliën en producten voor dagelijkse basisbehoeften. Deze CBB vormen de ruggengraat van de chemische sector.

De productie van CBB kan worden gedefossiliseerd door alternatieve koolstofbronnen (ACS) zoals CO_2, biomassa en plastic afval als grondstoffen te gebruiken. Het veranderen van de grondstof voor de productie van CBB is echter niet beperkt tot het veranderen van een bepaalde technologie, aangezien CBB over het algemeen worden geproduceerd in sterk met elkaar verbonden petrochemische clusters. Petrochemische clusters zijn geografische concentraties van verwante en/of direct met elkaar verbonden industrieën. Ze bieden concurrentievoordelen in termen van gedeelde infrastructuur, kennis, materialen en/of energie. Veranderingen in grondstoffen kunnen daardoor domino-effecten veroorzaken in de onderling verbonden waardeketens. Het identificeren en kwantificeren van dergelijke domino-effecten op proces- en clusterniveau was de focus van dit proefschrift.

Het overkoepelende doel van dit proefschrift was **het begrijpen van de impact van defossilisatie van de productie van chemische bouwstenen in bestaande petrochemische clusters**. Om deze vraag te beantwoorden, werden drie deelonderzoeksvragen geformuleerd, zoals hieronder weergegeven.

Hoe kan het gebruik van alternatieve koolstofbronnen (ACS) de productie van chemische bouwstenen in bestaande petrochemische clusters beïnvloeden?	
Deelonderzoeksvragen (SRQ)	SRQ-1: Hoe kunnen veelbelovende ACS-gebaseerde procesroutes op verschillende TRL-niveaus worden gescreend voor de productie van chemische bouwstenen?
	SRQ-2: Wat zijn de techno-economische gevolgen van het gebruik van ACS-gebaseerde technologieën voor de productie van chemische bouwstenen in bestaande petrochemische clusters?
	SRQ-3: Hoe beïnvloedt de beschikbaarheid van alternatieve koolstofbronnen potentiële technologieportfolio's voor de defossilisatie van de productie van chemische bouwstenen in bestaande petrochemische clusters?

De referentie- en ACS-gebaseerde technologieën werden gemodelleerd in Aspen Plus met een procesontwerp, operationele capaciteit en procescomplexiteit vergelijkbaar met die van de huidige CBB-productie-installaties in de haven van Rotterdam (PoR), Nederland. De technologieën werden vervolgens beoordeeld aan de hand van key performance indicators (KPI's) op zowel proces- als clusterniveau. Tot slot evalueerde dit proefschrift het technologieportfolio dat nodig is voor de defossilisatie van de CBB-productie (methanol, ethyleen, propyleen, benzeen, p-xyleen) en onderzocht het hoe beperkingen in de beschikbaarheid van ACS-grondstoffen het ontwerp en de prestaties van een gedefossiliseerd brownfield-petrochemisch cluster kunnen beïnvloeden. De belangrijkste bevindingen van het onderzoek zijn als volgt:

Screening van veelbelovende ACS-gebaseerde procesroutes op verschillende TRL-niveaus voor de productie van chemische bouwstenen

Gegeven de noodzaak om de petrochemische sector te defossiliseren, zijn momenteel veel mogelijke procesroutes die gebruikmaken van ACS in ontwikkeling. Zo zijn er bijvoorbeeld meer dan 65 verschillende ACS-gebaseerde procesroutes in de literatuur geïdentificeerd voor de productie van ethyleen. Deze vele opties bevinden zich in verschillende technological readiness levels (TRL), waardoor de selectie van een veelbelovende procesroute een complexe taak is.

Voor de selectie van veelbelovende ACS-technologieën werd een screeningmethodologie op basis van het stage-gate-concept ontwikkeld. De methode maakte gebruik van ideale stoichiometrische reacties en thermodynamische toestandsfuncties bij standaardtemperatuur- en drukcondities, met efficiëntie van koolstofbenutting, elektriciteits- en warmtebehoefte als belangrijke prestatie-indicatoren.

Uit de beoordeling bleek dat de C:H:O-verhouding van de ACS-grondstoffen een belangrijke rol speelde in de technische prestaties van het proces, aangezien een hoger zuurstofgehalte in de grondstof resulteert in een lagere efficiëntie van koolstofbenutting of een hogere waterstofbehoefte. Zo hebben CO_2, biomassa en plastic afval een zuurstofgehalte van 73, 49 en 0 gewichtsprocent (gew%). Omdat CO_2 het hoogste zuurstofgehalte heeft vereist het de hoogste energie-input voor zuurstofverwijdering door middel van hydrogenering of elektrochemische reductie voor CBB-productie. Plastic afval, dat een vergelijkbare C:H:O-samenstelling heeft als de op fossiele brandstoffen gebaseerde grondstoffen, scoorde beter dan biomassa- en CO_2-gebaseerde technologieën in de screeningmethodologie.

De resultaten toonden ook aan dat aannames met betrekking tot de oorsprong van waterstof een significante invloed hebben op de rangschikking van technologieën. Wanneer bijvoorbeeld wordt aangenomen dat waterstof wordt geïmporteerd, identificeerde de screeningmethodologie exotherme technologieën gebaseerd op de hydrogenering van CO_2 tot methanol en zuurstofvergassing van biomassa of plastic afval als de meest geschikte routes voor verder onderzoek. Als de waterstofproductie echter ter plaatse plaatsvindt, werden directe elektrochemische reductie, stoomvergassing van biomassa en pyrolyse van plastic afval hoger gerangschikt dan de bovengenoemde exotherme routes, wat betreft materiaal- en energie-efficiëntie. Dit komt doordat de materiaal- en energielasten van de energie-intensieve waterstofproductieprocessen niet zijn meegenomen in het geval van waterstofimport.

Dit onderzoek toont aan dat een relatief eenvoudige, op stoichiometrie gebaseerde stage-gate-methode kan worden gebruikt voor technologiescreening en dat aannames over de herkomst van waterstof R&D-portfolio's aanzienlijk kunnen veranderen.

Technisch-economische gevolgen van het gebruik van ACS-gebaseerde technologieën voor de productie van chemische bouwstenen in bestaande petrochemische clusters

Wanneer processen op basis van fossiele grondstoffen in onderling verbonden industriële clusters worden vervangen, kan dit gevolgen hebben voor de toeleveringsketens, downstream-eenheden, energie-eilanden en afvalverwerkingsinstallaties, maar ook voor de algehele prestaties van een cluster. Dit aspect is echter in de literatuur over het hoofd gezien. Om deze lacune in de literatuur aan te pakken, werd de impact van de ACS-gebaseerde productieroutes (geselecteerd met behulp van de screeningmethodologie) geanalyseerd op clusterniveau door veranderingen in massa, energie, prijzen, CO_2-uitstoot en waterbehoefte te beoordelen. De resultaten toonden aan dat, vanwege de significante verschillen in productdistributie, energiebehoefte en afvalproductie van ACS-gebaseerde processen, het petrochemische cluster aanzienlijke aanpassingen zal moeten ondergaan, zowel wat betreft massa- als energiestromen.

Op procesniveau, waren de belangrijkste uitdagingen voor de defossilisatie van olefinen en aromaten (i) de toegang tot grote hoeveelheden hernieuwbare elektriciteit tegen lage prijzen, met name voor waterstofproductie, en (ii) de hoge investeringskosten van ACS-gebaseerde processen in vergelijking met technologieën op basis van fossiele brandstoffen. Over het algemeen presteerden technologieën op basis van plastic afval beter dan technologieën op basis van biomassa en CO_2, vanwege de betere C/H-verhouding van de grondstof. Dit leidde tot een lagere externe waterstofbehoefte en hogere productopbrengsten.

Voor olefinen vormde de vervanging van de naftakraker door ACS-gebaseerde technologieën een aanzienlijke uitdaging op clusterniveau. Dit komt voornamelijk door verschillen in productprofielen en de noodzaak van ingrijpende veranderingen in de infrastructuur voor elektriciteit, water en afvalverwerking. Gemiddeld verbruikten de in dit proefschrift bestudeerde ACS-processen 5 tot 10 keer meer elektriciteit en water per geproduceerde eenheid ethyleen. Het significante verschil in behoefte aan utilities zou een ingrijpende herstructurering van utilities vereisen om de ACS-gebaseerde processen in het cluster te integreren. De gevolgen van defossilisatie voor de structuur van het cluster waren merkbaar door het verschil in de verhouding tussen product en bijproduct (vooral voor propyleen, afgas en zware koolwaterstoffen in de ACS-gevallen). Dit gold met name voor het CO_2-gebaseerde directe elektrochemische reductieproces voor de productie van ethyleen, waarbij geen propyleen wordt geproduceerd. Hierdoor zou propyleen geïmporteerd moeten worden, wat logistieke en milieuproblemen met zich mee zou brengen als het propyleen bijvoorbeeld van fossiele oorsprong zou zijn.

Voor de productie van aromaten was de route van methanol naar aromaten op basis van plastic afval, van de ACS-gebaseerde routes, het meest concurrerend en had de minste impact op clusterniveau. Op clusterniveau werden de belangrijkste verschillen tussen de processen waargenomen in de productie van xyleen, de productie van afgassen, het elektriciteits- en waterverbruik en de infrastructuur voor afvalverwerking. Significante verschillen in de behoefte aan utilities waren voornamelijk te wijten aan de hoge waterstofbehoefte en de hogere benodigde druk voor het methanolproductieproces in vergelijking met de bestaande fossiele processen. De hogere waterbehoefte werd veroorzaakt door de waterelektrolyse en het stoomvergassingsproces voor de productie van syngas om methanol te produceren.. Ongeveer 80-90% van zowel de elektriciteitskosten als de investeringskosten (CAPEX) werden toegeschreven aan het ACS-proces voor methanolproductie. Voor het op ACS gebaseerde aromatenproces speelde de technisch-economische prestatie van het methanolproductieproces dus een cruciale rol, zowel op proces- als op clusterniveau.

De integratie van ACS-technologieën resulteerde in een lager gehalte aan fossiele koolstof en aanzienlijke prijsveranderingen in de waardeketen. Zo zou een prijsverandering van +134% in de levelized cost van ethyleen als gevolg van een ACS-proces alleen al leiden tot een prijsstijging van 97% voor polyvinylchloride en een prijsstijging van 34% voor polyethyleentereftalaat. De uiteenlopende prijseffecten in de waardeketen waren te wijten aan verschillen in de benodigde CBB in de productieprocessen, referentieprijzen en procesopbrengsten. Van de verschillende olefinen- en aromatenketens bleken polyvinylchloride, aceton, cyclohexaan en polyethyleentereftalaat het meest beïnvloed te worden, zowel wat betreft het bereiken van de hoogste mate van defossilisatie als de grootste prijseffecten. Dit komt doordat in deze waardeketens respectievelijk 80% tot 100% van de embedded koolstof afkomstig is van olefinen en aromaten. Vergeleken met de defossilisatie van olefinen resulteerde de defossilisatie van aromaten in de grootste verandering van embedded koolstof in het cluster, aangezien aromaten meer dan 50% van de embedded koolstof in het cluster vertegenwoordigen.

Voor zowel ACS-gebaseerde olefinen- als aromatenprocessen leidde de grote elektriciteitsbehoefte, het waterstofverbruik en de afvalproductie tot andere effecten, zoals een hoger waterverbruik, afvalwaterproductie en CO_2-uitstoot. Indien deze niet adequaat worden aangepakt, kunnen ze het doel van de defossilisatie van chemische bouwstenen tenietdoen. De analyse toonde aan dat verdere verbeteringen in afvalvalorisatie en de integratie van hernieuwbare energie nodig zijn om het klimaatvoordeel van ACS-gebaseerde technologieën te waarborgen. ACS-gebaseerde technologieën moeten daarom worden ingezet in combinatie met op hernieuwbare energie gebaseerde utilities en afvalwaterzuiveringsinstallaties om het systeem koolstofarm te maken en de waterstress te verminderen.

Impact van de beschikbaarheid van alternatieve koolstofbronnen op de potentiële technologieportfolio's voor de defossilisatie van de productie van chemische bouwstenen in bestaande petrochemische clusters

Voor de productie van dezelfde hoeveelheid CBB zijn grotere hoeveelheden ACS-gebaseerde grondstoffen nodig in vergelijking met fossiele grondstoffen, vanwege het lage koolstof- en waterstofgehalte van ACS-gebaseerde grondstoffen. De beschikbaarheid van ACS beïnvloedt niet alleen de mate waarin een petrochemisch cluster kan worden gedefossiliseerd, maar ook het technologieportfolio dat nodig is voor de CBB-productie. In deze studie werd het technologieportfolio dat nodig is voor de defossilisatie van een brownfield petrochemisch cluster geanalyseerd, rekening houdend met twee doelstellingen: (i) minimalisering van het gebruik van fossiele koolstof en (ii) minimalisering van de CAPEX-penalty (gedefinieerd als de som van de nieuwe investeringen plus het verlies aan CAPEX als gevolg van het verwijderen van bestaande activa) om de verandering in de bestaande infrastructuur te beperken. Er werden drie casussen onderzocht: een referentiecasus en twee casussen gedefinieerd door de beschikbaarheid van ACS-grondstoffen, één zonder beperkingen en één met beperkte beschikbaarheid.

Een vergelijking van de technologieportfolio's tussen de onbeperkte en beperkte ACS casussen liet een variatie zien van 2 tot 8 keer in de CAPEX-penalty, energieschattingen en waterbehoefte. Het bereiken van een defossilisatiegraad van 95% resulteerde in een aanzienlijke CAPEX-penalty van circa € 33 miljard, naast een elektriciteitsbehoefte van 65 PJ per jaar. Dit staat in schril contrast met het referentiescenario, dat slechts € 2 miljard aan CAPEX en 7 PJ per jaar aan elektriciteit vereiste. Bovendien steeg de waterbehoefte in het cluster van 2 miljoen ton per jaar in het referentiescenario naar 14 miljoen ton per jaar in het defossilisatiescenario met onbeperkte beschikbaarheid van grondstoffen, voornamelijk als gevolg van het stoomvergassingsproces dat wordt gebruikt om plastic afval via syngas om te zetten in methanol. Om tot 95% defossilisatie te bereiken voor de productie van chemische bouwstenen, zou ongeveer 19.5 miljoen ton plastic afval per jaar nodig zijn, wat meer dan drie keer zoveel is als de huidige plasticproductie in Nederland. Wanneer er voldoende plastic afval beschikbaar was, werd van de op plastic afval gebaseerde ACS-technologieën het methanolproces geselecteerd, omdat methanol zowel in olefinen als in aromaten kon worden omgezet.

Toen beperkingen in de grondstoffen in het model werden meegenomen, werd een maximale defossilisatie van 55% van de CBB-productie bereikt. Dit scenario vereiste ongeveer 200 PJ/jaar elektriciteit, 3 Mt/jaar CO_2, 8 Mt/jaar biomassa en 7 Mt/jaar plastic afval. De olefinenproductie werd gedeeltelijk gedefossiliseerd met behulp van synthetische nafta uit pyrolyse van plastic afval, de aromatenproductie werd gedefossiliseerd met een methanol-naar-aromatenproces en de waterstofproductie werd gedefossiliseerd met behulp van waterelektrolyse. De studie schatte dat er een CAPEX-penalty van ongeveer 35 miljard euro zou worden opgelopen om tot 55% van het cluster te defossiliseren, wat ongeveer 18 keer de CAPEX van de op fossiele brandstoffen gebaseerde CBB-productie-installaties in het model is, vanwege de noodzaak om duurdere technologieën in te zetten. De waterbehoefte in het cluster steeg van 2 miljoen ton per jaar in het referentiescenario naar 8 miljoen ton per jaar, voornamelijk als gevolg van het stoomvergassingsproces datplastic afval en biomassa omzet in methanol via syngas en hydrogenering van CO_2 tot methanol. De resultaten wijzen erop dat, gezien de beperkingen van ACS-grondstoffen en de huidige vraag naar CBB, een combinatie van ACS- en fossiele technologieën naast elkaar zal moeten bestaan. Er is geen enkel proces of grondstof die de CBB-productie volledig kan defossiliseren; een combinatie van ACS-grondstoffen zal nodig zijn.

Dit onderzoek wijst erop dat de beperkingen in de beschikbaarheid van ACS-grondstoffen een aanzienlijke impact zullen hebben op de prestaties van bestaande brownfield industriële clusters. De omvang van de benodigde energie en materiaal voor een dergelijke verandering laat zien dat een grote uitdaging voor bestaande petrochemische clusters, vergelijkbaar met de haven van Rotterdam, de 5 tot 10 keer hogere elektriciteits- en waterbehoefte zal zijn. Dit betekent dat ofwel de productiecapaciteit van chemische processen moet worden afgeschaald, ofwel strategische beslissingen moeten worden genomen over welke chemische stof in het cluster geproduceerd moet worden. Een andere optie is het importeren van hernieuwbare koolstofhoudende tussenproducten zoals methanol, pyrolyseolie, ethanol of Fischer-Tropsch-nafta naar het cluster. Omdat deze processen echter zeer energie-, investerings- en grondintensief zijn, kan deze verschuiving leiden tot een toenemende milieubelasting buiten Nederland, wat nader onderzocht moet worden.

1. Introduction

Chapter specific nomenclature & symbols

Nomenclature

ACS	Alternative carbon source
BTX	Benzene, toluene & xylene
CBB	Chemical building block
DME	Dimethyl ether
EDC	Ethylene dichloride
FLASC	Fast Life Cycle Assessment of Synthetic Chemistry
HC	Hydrocarbon
KG	Knowledge gap
MDI	Methylene diphenyl diisocyanate
MTBE	Methyl tertbutyl ether
MXDA	m-xylene diamine
NREL	National Renewable Energy Laboratory
PET	Polyethylene terephthalate
PO	Propylene oxide
PoR	Port of Rotterdam
PTA	Pure terephthalic acid
PVC	Polyvinyl chloride
SBA	Secondary butyl alcohol
SM	Styrene monomer
SRQ	Sub-research question
TBA	Tertbutyl alcohol
TEA	Techno-economic analysis
TRL	Technology readiness level
VCM	Vinyl chloride monomer

1. Introduction

Today's everyday products such as plastics, cosmetics, synthetic fibers, adhesives, fertilizers, chemicals and fuels, are produced by the petrochemical industry from fossil fuels[1] (e.g., naphtha, natural gas, coal and ethane). Chemical value chains in the petrochemical industries often start with the conversion of carbon-based feedstocks (e.g., naphtha derived from crude oil) into high-volume chemicals like ethylene, propylene, benzene and p-xylene. These high-volume chemicals are the backbone of the petrochemical industry and are known as chemical building blocks (CBB). They are used as the primary feedstock in the production of other chemicals and materials (intermediate and end-of-value chemicals) as shown in Figure 1. Based on the chemical nature of the CBB, they can be classified into syngas-based (methanol, ammonia and carbon monoxide), olefins (ethylene, propylene and butadiene) and aromatics (benzene and xylene).[2]

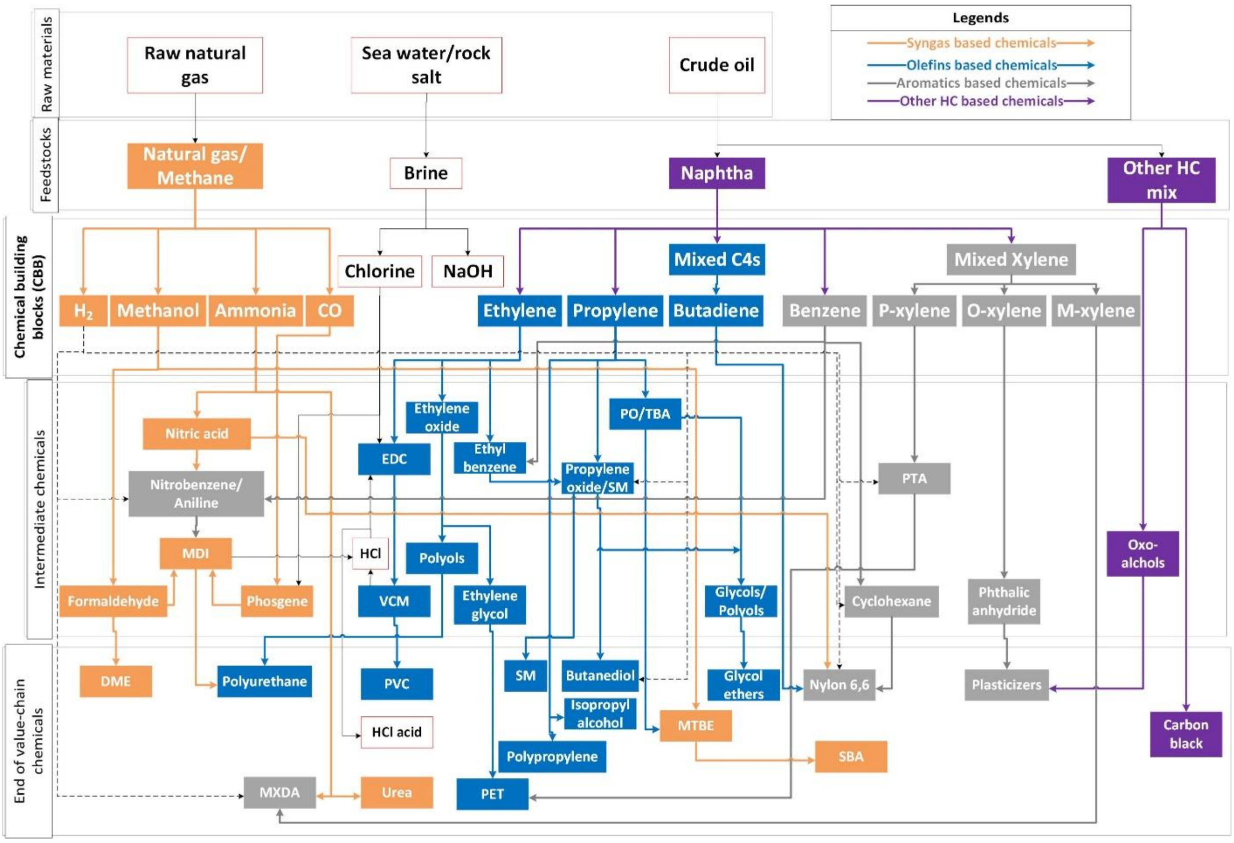

Figure 1: Simplified diagram including four value chains in a petrochemical cluster, grouped in different colours (Abbreviations: HC- Hydrocarbon, MDI- Methylene diphenyl diisocyanate, DME- Dimethyl ether, EDC- Ethylene dichloride, VCM- Vinyl chloride monomer, PVC- Poly vinyl chloride, PET- Polyethylene terephthalate, SM- Styrene monomer, MTBE- Methyl tertbutyl ether, PTA- Purified terephthalic acid, PO- Propylene oxide, TBA- Tertbutyl alcohol, MXDA- m-xylene diamine, SBA- Secondary butyl alcohol).

The production of petrochemicals accounts for about 6% of the global CO_2 emissions and their demand is forecasted to double by 2050.[3] As these chemicals are currently produced from fossil-based feedstocks, using energy intensive production processes, it will be difficult for our society to reach the net-zero emission targets without reducing their carbon footprint.[3,4] It is important to note that fossil-based feedstocks are not only used as fuels, but also as a carbon source for the products, as most chemicals contain carbon embedded in their molecules. Therefore, decarbonising the feedstocks in the petrochemical industries is not possible. However, the production of CBB can be decoupled from the oil and gas industry by replacing the fossil carbon with alternative carbon sources (ACS)[2–4] namely CO_2, biomass, or plastic waste [2,5], which is referred to as defossilisation.[6]

Using ACS feedstocks opens a large number of possibilities for defossilising CBB production.[5,7,8] However, the wide range of options, which are at different levels of technology readiness, makes identifying promising ACS-based technologies challenging, considering existing infrastructure, demand, a desired net-zero future, and a transition situation between both.

1.1. Technology screening

With the advancements in modern chemistry and the need to defossilise the petrochemical industry, a large number of possibilities are being developed that use ACS to produce chemicals through electrochemical, biochemical, thermochemical, or catalytic processes.[5,7,8] The existence of various potential routes makes the selection of alternatives a complex task that relies on multiple techno-economic and environmental criteria. Conventionally, selecting the feedstock and process route for a given product is driven by considerations regarding feedstock (availability and cost), expenditures (capital and operational), by-product demand, environmental regulations, reliability, and safety.[7,9] Thus, a comprehensive techno-economic and environmental assessment for technology screening, will need a significant amount of information and time.

In technology screening, short-cut screening methodologies are used first to identify promising technologies, which can then be evaluated with a more thorough assessment. Examples of short-cut methods are the Environmental Hazard Index[10], Waste Reduction algorithm[11], GSK Green chemistry measure approach[12], Environmental-factors[13], Global Material Economy[14] and stoichiometry-based targeting[15]. They use initial estimates of waste production, energy usage and/or efficiency (based on preliminary data on chemical reaction, process conditions, and yield) to compare and select promising technologies. Table 1 shows short-cut screening methods that have been used for screening and identifying promising feedstocks and technologies in the petrochemical industry.

Table 1: Short-cut screening methods and examples of carbon feedstocks and chemicals considered in the cited references.

Short-cut methods	**Carbon feedstock**	**Screened chemicals**
Environmental Hazard Index[10]	Tert-butyl alcohol, isobutylene, propylene, ethylene, acetone cyanohydrin	Methyl methacrylate
Waste reduction algorithm[11]	Secondary butyl alcohol	Methyl ethyl ketone
GSK green chemistry measure approach[12]	Aromatics compounds	Chemicals for pharmaceutical industry
Environmental factors[13]	Syngas	Methanol, ethanol and ethylene
Global material economy[14]	C1-C24 hydrocarbon fragments	Discodermolide
Stoichiometry-based targeting[15–17]	CO_2	Methane, methanol, ethanol and other speciality chemicals
Thermodynamics-based method[18–20]	Cellulose, CO_2	Carbon, methane, methanol, ethanol, ethylene, propylene oxide and other speciality chemicals
GSK Fast Life Cycle Assessment of Synthetic Chemistry (FLASC) [21]	Aliphatic and aromatics hydrocarbons	Solvents for pharmaceutical industry
BASF Eco-efficiency analysis[22,23]	Indigo	Dyeing products

Taxonomical and technical barriers method[24]	Sugars (like glucose, fructose, xylose, sucrose) and syngas	Methanol, ethanol and other speciality chemicals
Eco-scale assessment[25]	Aromatic hydrocarbons	Solvents like aniline, benzoic acid
Proxy indicator approach[26–33]	Syngas, sugars, ethanol and glycerol	Biodiesel, butadiene, acetone, ethylene and propylene

Although short-cut screening studies shortlist a wide variety of chemical technologies, generally only one type of ACS feedstock is considered in detail and the studies have not been used for a comprehensive analysis. For instance, in the taxonomical and technical barriers method[24] proposed by the National Renewable Energy Laboratory (NREL), from a list of more than 300 technologies, they selected twelve options for the production of chemicals like methanol, or sorbitol, all using biomass-based feedstocks. The study did not consider CO_2 or plastic waste feedstocks and focused on selecting technologies for specialty chemicals rather than CBB. The studies by Otto et al.,[16] Chauvy et al.,[17] Pacheco et al.,[19] and Cui et al.,[20] used the stoichiometry-based targeting and the thermodynamics-based methods, for screening CO_2 based technologies to find promising chemicals that can be produced. Their studies[16,17,19,20] did not consider biomass or plastic waste feedstocks and focused on finding promising technologies, which could use ACS feedstocks for the production of a wide variety of generic chemicals.

Among the short-cut screening studies; the work by Ren et al.,[34] Patel et al.,[30] Posada et al.,[33] and Moncada et al.,[31] were the only studies that focused on screening CBB. However, in their works, only biomass-based feedstocks were selected for CBB production. ACS feedstocks like CO_2 and plastic waste were not considered in any of these studies. Therefore, the short-cut screening studies have not been used to screen in a comprehensive manner considering all ACS feedstocks for the production of CBB (i.e., considering CO_2, biomass and plastic waste for the production of syngas based, olefins and aromatics).

Therefore, a technology screening study to compare and select promising technologies for the production of CBB (methanol, ethylene, propylene, benzene and p-xylene) considering ACS feedstocks (CO_2, biomass and plastic waste) is needed to provide a harmonised understanding about promising ACS-based technologies.

1.2 Process and cluster level impact assessment of defossilisation

Technologies selected from a technology screening step are often at different technology readiness levels (TRL) and thus, they cannot be easily compared due to the dissimilarity in data availability, production scales and uncertainties associated with early-stage technologies. To address this issue, ex-ante techno-economic assessment (TEA) can be used. Ex-ante TEA refers to the assessments in which low TRL technologies are analysed assuming they are scaled-up to commercial scale (TRL 9). The results are exploratory in nature[35] and it has been widely applied for analysing ACS-based technologies.[36–39]

Several studies have used an ex-ante TEA to assess process level techno-economic impacts of defossilising CBB production. As an illustration of the type of assessments, three studies are discussed here. Sharifzadeh et al.,[40] studied the technical and economic feasibility of using biomass-based pyrolysis oil as a substitute for fossil-based naphtha in the production of CBB. The study showed that with a minimal retrofit of the naphtha cracker with a catalytic bio-oil reactor, the existing downstream separation processes could be used to produce CBB, increasing the minimum selling price by two compared to the reference case. Ioannou et al.,[41] compared the production of ethylene from CO_2 by direct electrochemical conversion and indirect thermochemical route (via methanol intermediate followed by methanol-to-olefin). They pointed out that the thermochemical indirect route currently appears to be economically and environmentally superior, due to the low efficiencies and high cost of

CO_2 electrolysers. Likewise for aromatics, Bazzanella et al [42] studied the production of benzene, toluene and xylene (BTX) from CO_2 and biomass, and compared it with conventional fossil-based routes. The study showed that methanol-to-aromatics-based routes using CO_2 and biomass required approximately 25 times more electricity than a conventional naphtha cracker to produce BTX, due to the large electricity demand for hydrogen production in the ACS-based routes.[42] Their economic analysis showed that the production cost of methanol-to-aromatics-based BTX was three times higher than the conventional fossil-based route.

The studies named above are limited to one-to-one comparisons between ACS-based feedstocks and their fossil-based counterparts and are studied as stand-alone processes (greenfield projects). However, the production of CBB generally occurs in petrochemical clusters. Petrochemical clusters are "*a spatial concentration or geographic agglomeration of related and/or directly connected industries*".[43(p.739)] They generally provide competitive advantages in terms of shared infrastructure, knowledge, materials, and or energy.[43] As illustrated in Figure 2, petrochemical clusters typically consist of crude oil refineries, CBB production plants, downstream processing plants (for production of intermediate chemicals, fine chemicals, pharmaceuticals, polymer production) and energy (heat, power) generation units concentrated in a geographic location.[43] Petrochemical clusters can be large; therefore, industries tend to group themselves into so called sub-clusters (industries in a sub-cluster tend to share the same supply chains of CBB)[43](see Figure 2). The sub-clusters can be further divided into value chains, which are a set of primary and intermediate industries that are required to produce specific end-of-value-chain products (like fine chemicals, polymers or pharmaceuticals).[44] In a petrochemical cluster, one or several value chains can exist, and they tend to share common flows of material, energy, infrastructure or products. Replacing feedstocks and/or technologies in such a complex network will affect not only the processes themselves (e.g., equipment, energy, water, utilities, safety) but also create impacts in the cluster through changes in products, by-products, waste and energy streams.[45] In a highly interconnected petrochemical cluster, these changes can result in cascading impacts similar to a domino effect.[46] In the context of this research, the domino effect is defined as the chain of negative or positive impacts in other industries (in terms of material, energy and/or economic exchange) caused by a change in one industry, resulting in cluster level impacts.

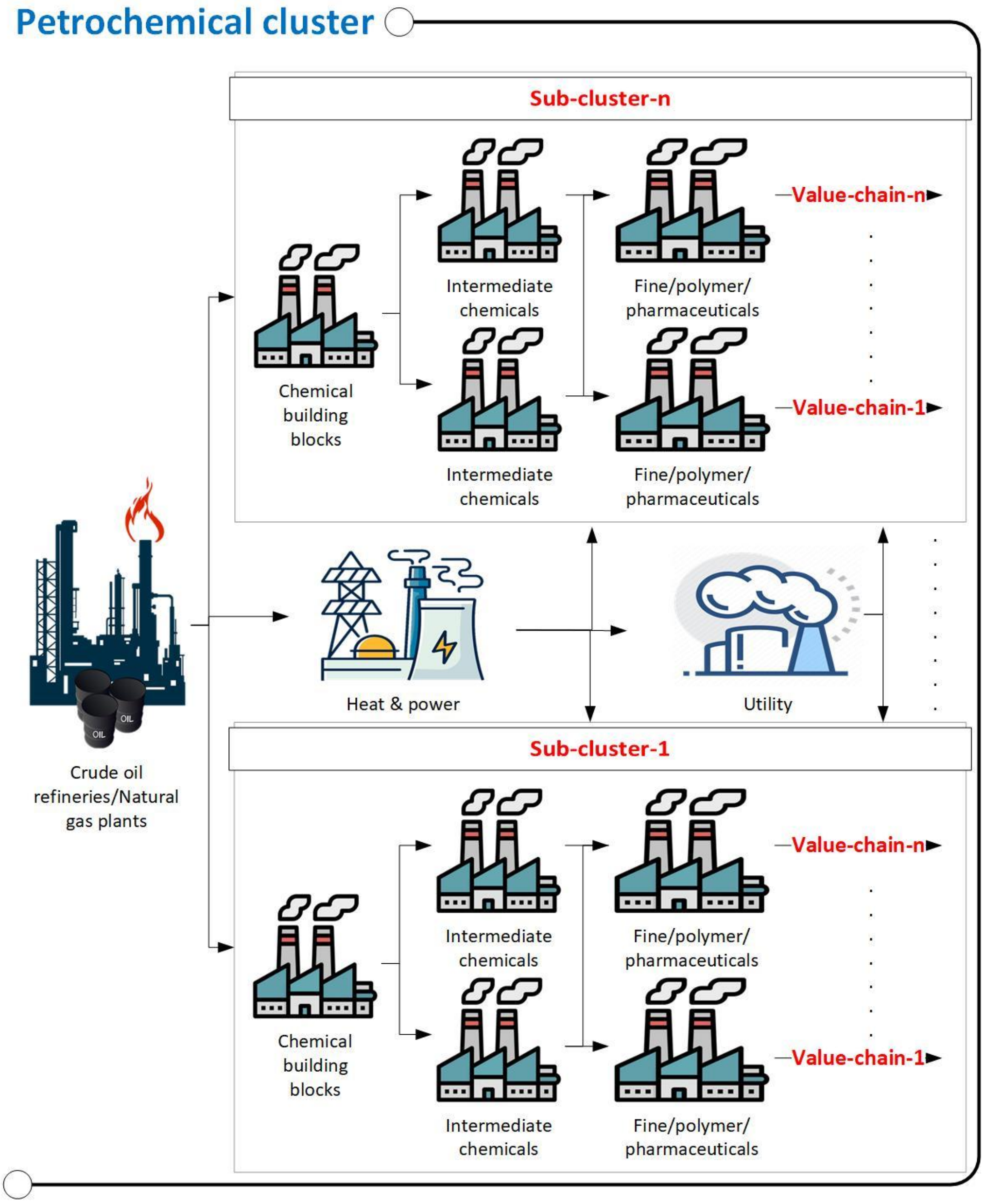

Figure 2: Simplified diagram of a petrochemical cluster

The existence, magnitude, and significance of domino effects due to the defossilisation of petrochemical clusters have been studied mainly from the energy perspective, while impacts, for instance, on materials flows and value-chain product prices have not been studied at the same level of detail. For example, Hackl et al.,[47,48] assessed the potential of integrating bio-based ethylene production in an existing petrochemical cluster (Stenungsund Chemical cluster, Sweden) by conducting a pinch point analysis. The study, combining plant data with Aspen process modelling data to conduct the energy assessment, concluded that the ethanol dehydration process could benefit from being in a petrochemical cluster compared to a standalone bio-ethylene process due to the excess high temperature heat available in the cluster site. However, the study did not consider the material or price impacts due to the bio-based ethylene production in the existing cluster. For the Stenungsund chemical cluster, Holmgren et al.,[49] used the model of Hackl et al., [47,48] to assess the potential of bio-methanol using the biomass gasification process in the petrochemical cluster for fuel and olefins production. Their study focused mainly on the energy integration of the ACS-based process with the existing system. They used pinch analysis to show that the integrated system resulted in a reduction of CO_2 emissions compared to the stand-alone bio-methanol process. These exemplify that domino effects on downstream units through material and prices changes due to defossilisation have received less attention than energy impacts, limiting a comprehensive understanding of the techno-economic impacts of defossilisation at a cluster level.

For the Port of Rotterdam (PoR) in the Netherlands, Schneider et al.,[50–52] developed an energy system model to analyse energy and feedstock decarbonisation options. Using publicly available data, they built black-box models for electricity generation, refineries, petrochemical processes (like stream cracker), and explored defossilisation options for the olefin production plant in the PoR.[52] They considered feedstocks like biomass and plastic waste, and technologies like water electrolysis, gasification, low-temperature Fischer-Tropsch, syngas hydrogenation-to-methanol and methanol-to-olefins. The study showed that by 2050, about 9 Mt of dry biomass, 3 Mt of plastic waste and 50 TWh of low-carbon electricity will be required to achieve carbon neutrality in the PoR petrochemical cluster.[52] Towards a comprehensive analysis, the study did not consider CO_2 as a feedstock or CBB like methanol and aromatics. Although their study[52] identified and qualitatively assessed five key challenges for feedstock defossilisation in petrochemical clusters, such as impact on energy providers, change in product portfolios, high investments needs, cost uncertainty of low TRL technologies and ACS feedstock availability,[52] it did not quantify the domino impacts.

It can be seen that the cluster level studies to date, have not considered CBB like methanol and aromatics to the same extent as olefins. Furthermore, the domino effects on downstream value chains, interconnected utility providers and waste treatment plants due to feedstock defossilisation for the production of CBB in an existing petrochemical cluster have not been quantified in the state-of-the-art.

1.3 Impact of ACS feedstock availability on technology portfolios

It can be seen from cluster level studies[50,53] that the availability of ACS is considered one of the key challenge, for defossilising petrochemical clusters. Several studies have discussed and quantified the amount of ACS required for defossilising CBB production at global, national and cluster levels; as discussed below.

At a global level, several studies have examined the challenges for transitioning the chemical industry away from fossil fuels. However, they have pointed out that a feedstock portfolio of CO_2, biomass, and plastic waste will be necessary, as each ACS has availability constraints.[3,54,55] For example, a study by the Royal Society estimated that achieving net-zero emissions in the chemical sector would require approximately 7000 Mt of wet biomass globally.[3] Only 4300 Mt of wet biomass is available globally (as of 2022) including agriculture residues, forest residues and the biogenic fraction of municipal waste.[3]

For plastic waste feedstock, globally, around 300 to 400 Mt of plastic are produced annually, yet only about 9% is recycled, creating a challenge for feedstock availability for the waste-to-chemical processes.[3] Regarding CO_2 feedstock, the estimated demand range is estimated at around 2800 Mt to 4700 Mt, which is less than 1% of global anthropogenic CO_2 emissions in 2022 (~59,000 Mt CO_2).[3] Although CO_2 availability would not be a limiting factor for chemical production, the primary challenge lies in the significant amount of (green) electricity required for its capture and the CO_2-based processes either for hydrogen production or direct electrochemical reduction.[56] Lopez et al[55] estimated that, by 2050, the global chemical sector would need between 40,000 TWh and 50,000 TWh of electricity to transition to a CO_2 dominant (i.e., 80% of carbon feedstock supplied by CO_2 and rest by biomass) chemical sector. Given that in 2023 the total global electricity generation was around 30,000 TWh[57], an additional supply equivalent to the current global production would be necessary for a CO_2-based chemical transition. Zanon-Zotin et al[54] estimated that due to limitations in biomass feedstock and renewable electricity availability, only 28% of the global primary chemical sector could be defossilised by 2050.

National level studies in Europe align with these findings, indicating that feedstock availability remains a significant obstacle. For instance, Hennig et al[58] pointed out that Germany could only meet 10% of the total primary energy consumption in 2013 through a sustainable bioenergy supply.[58] Schijndel et al.[59] examined a portfolio of technologies that included electrolysis, pyrolysis, gasification, fermentation, Fischer-Tropsch and methanol synthesis for the Dutch chemical production. They indicated that by 2050, around 300 TWh of renewable electricity, 35 Mt of biomass and recycled plastic will be needed for its defossilisation. However, the total electricity production is around 120 TWh[60] and the available sustainable biomass and plastic waste are around 14 Mt[61,62] in the Netherlands, which shows the potential magnitude of energy and material required for the transition of the Dutch chemical industry. At a cluster level, Lucas et al[53] assessed the potential of ACS feedstocks for transitioning the PoR in the Netherlands. They estimated that biomass, bio-oils, plastic waste, and pyrolysis oil-based technologies would require 34 times more electricity than the current demand and could replace only up to 40% of the total carbon feedstock demand in the PoR petrochemical cluster.[53] This limitation is caused by the lower energy densities and conversion efficiencies of ACS compared to fossil-based alternatives.[53] Although the study by Lucas et al[53] provide valuable insights into the quantities of ACS required and the extent to which the PoR cluster can be defossilised, there is a gap in knowledge regarding how the technological portfolio changes under such constraints and how it affects the performance of the cluster.

2. Knowledge gaps

Three knowledge gaps were identified in the research field, as shown in Table 2.

Table 2: Identified knowledge gaps

Knowledge Gap (KG)	
KG-1	Lack of harmonised screening studies to select promising technologies from alternative carbon sources (ACS) like CO_2, biomass and plastic waste at different TRLs for the production of chemical building blocks.
KG-2	Lack of understanding of potential impacts on existing petrochemical clusters for defossilising the production of chemical building blocks.
KG-3	Limited insights into how ACS availabilities could affect technology portfolios to defossilise the production of chemical building blocks in existing petrochemical clusters.

3. Research questions

Based on the identified knowledge gaps, a main research question and three sub-research questions (SRQ) were formulated as shown in Table 3. The overarching aim of the thesis is to gain understanding of **the potential impacts of defossilising the production of chemical building blocks in existing petrochemical clusters**.

Table 3: Research questions of the thesis (Abbreviation: KG- Knowledge gap)

How can the use of alternative carbon sources (ACS) affect the production of chemical building blocks in existing petrochemical clusters?		
Sub-research questions (SRQ)	*SRQ-1: How to screen promising ACS-based process routes at different TRLs to produce chemical building blocks?*	*KG-1*
	SRQ-2: What are the techno-economic impacts of using ACS-based technologies for the production of chemical building blocks in existing petrochemical clusters?	*KG-2*

	SRQ-3: How does the availability of alternative carbon sources affect potential technology portfolios for defossilising the production of chemical building blocks in existing petrochemical clusters?	*KG-3*

The answers to the research questions were addressed by a combination of technology screening, process modelling and ex-ante techno-economic impact assessment at both process and cluster levels.

4. Dissertation outline

This dissertation is arranged into seven chapters, including the introduction chapter, as follows:

Chapter 2: This chapter answers the first research (SRQ-1) question. It explores more than fifty ACS-based processes for the production of ethylene and presents a technology screening methodology based on a stage-gate selection method. Ideal stoichiometric reactions and thermodynamic state functions were used to calculate key performance indicators like carbon utilisation efficiency and energy needs. This chapter, illustrates the screening methodology by comparing the three ACS to select ACS-based technologies for the production of ethylene. The chapter also addresses the topic of cascading price change impacts and extent of defossilisation in value chains due to the use of an ACS-based production process in an ethylene cluster.

Chapter 3: This chapter is an extended work of Chapter 2 and contributes to answering the SRQ-1 by exploring why hydrogen origin matters when screening ACS-based technologies. It explores more than seventy ACS-based ethylene production routes considering process hydrogen, green hydrogen, blue hydrogen and hydrogen import using the screening methodology of chapter-2. The chapter discusses how factors such as ACS-based feedstock's hydrogen content and assumptions regarding hydrogen availability affects technology screening.

Chapter 4 and Chapter 5: These chapters answer the second research question (SRQ-2) by assessing the process and cluster level impacts of defossilising olefins production (Chapter 4) and aromatics (Chapter 5) in an existing petrochemical cluster. Six ACS-based olefins production processes and three ACS-based aromatics production processes were selected in Chapters 4 and 5 respectively, using the screening methodology developed in Chapter 2. The technologies were studied by assessing changes in mass, energy, prices, CO_2 emissions, and water demand compared to the reference case petrochemical cluster. The reference case considered in this research is a representative cluster with complexities and capacities similar to the petrochemical cluster in the Port of Rotterdam. The ripple effects on downstream units, utility providers and waste treatment plants due to feedstock defossilisation are examined in these chapters.

Chapter 6: This chapter answers the final research question (SRQ-3). Data from Chapter 4 and Chapter 5 are used to examine the potential technology portfolios required for defossilising the production of CBB processes (i.e., methanol, olefins and aromatics) in the reference case petrochemical cluster. Twelve ACS-based technologies were assessed using three cases, i.e., a reference case, a case without feedstock limitations and a case where feedstock availability is limited. The technology portfolios were optimised to decrease the use of fossil carbon while minimising new CAPEX investments in the cluster.

Chapter 7: The final chapter concludes the dissertation by summarising the findings and providing an answer to each research question. It also points out the limitations of this dissertation and provides recommendations for future work.

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

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Chapter specific nomenclature & symbols

Nomenclature	
ACS	Alternative carbon source
BSG	Biomass steam gasification
CBB	Chemical building block
CKI	Chlorine waste incineration
CUE	Carbon utilisation efficiency
DER	Direct electrochemical reduction
EB	Ethylbenzene
EC	Economic constraint
EDC	Ethylene dichloride
EG	Ethylene glycol
EO	Ethylene oxide
FT	Fischer Tropsch
MTO	Methanol to olefin
PET	Polyethylene terephthalate
PO	Propylene oxide
PPI	Producer prices indices
PVC	Polyvinyl chloride
SM	Styrene monomer
TRL	Technology readiness level
VCM	Vinyl chloride monomer
Symbols	
ΔG^0	Standard Gibbs energy change
ΔH^0	Standard enthalpy change
ΔS^0	Standard entropy change

Abstract

Due to the heavy dependence on fossil-fuels as raw materials, the defossilisation of feedstocks in the petrochemical industry represents a challenge. A large number of possible process routes that use alternative carbon sources (ACS) like CO_2, 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 defossilising one value-chain can have cascading effect on other value-chains as observed for PET.

1. Introduction

Europe has set the ambitious goal to be carbon-neutral by 2050 and feedstock defossilisation of carbon-based industrial processes is challenging.[5] 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 CO_2, biomass and waste is considered an option for the replacement of oil and gas feedstocks.[7] A large number of possible processes using ACS are being developed to produce chemicals through electrochemical, biochemical, and thermochemical routes.[8] 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 CO_2 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:

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

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

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

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

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.

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

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 (CO_2 and biomass) were selected.

2.2 Base-case ethylene cluster model

This chapter 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 chapter. The corresponding mass flows used as reference in this study are depicted in Figure 1.

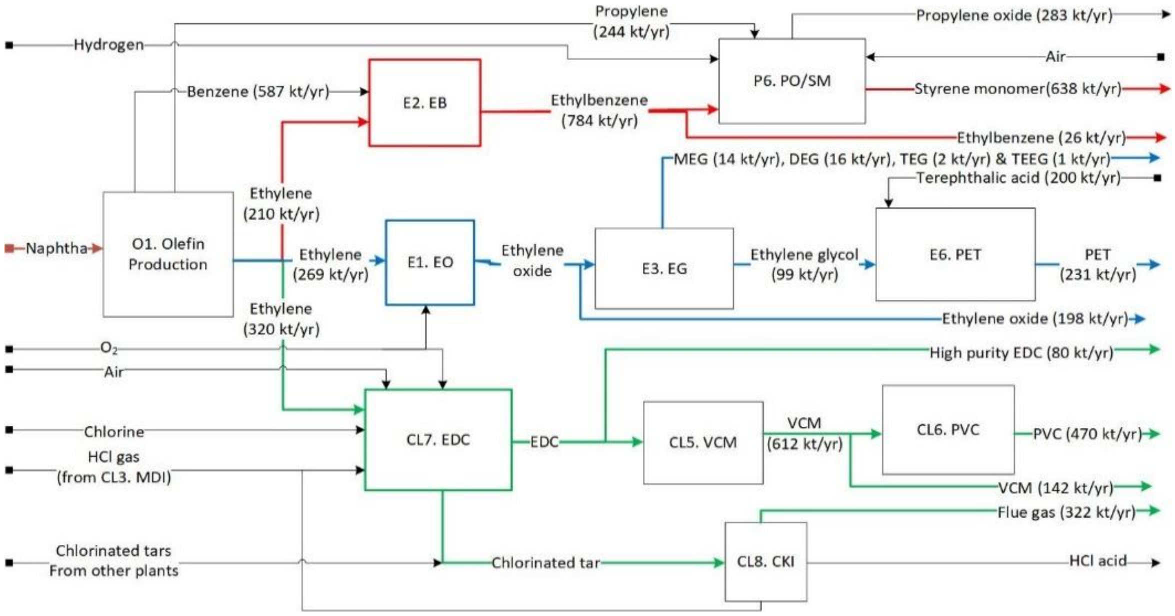

Figure 1: Simplified ethylene cluster with main mass flows

2.3 Value chain impact propagation

2.3.1 *Feedstock defossilisation impact on value chain*

In this study, value chain defossilisation is defined as the replacement of fossil-based raw materials with ACS carbon-based raw materials. To understand the extend of the defossilisation 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).

$$CBB\ carbon\ contribution = \frac{CBB\ carbon\ atoms}{Value\ chain\ product\ carbon\ atoms} \tag{5}$$

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 utilisation efficiency was also evaluated. The value chain carbon utilisation 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.

$$Value\ chain\ CUE = \frac{Value\ chain\ chemical\ carbon\ mass\ flow}{\sum_{CBB} Carbon\ mass\ flow} \tag{6}$$

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).

$$Gross\ margin = Revenue_{base\ case} - OPEX_{base\ case} = Revenue_{ACS\ case} - OPEX_{ACS\ case} \tag{7}$$

$$\sum_{Products} \Delta Price * Mass\ flow = \sum_{Raw\ materials} \Delta Cost * Mass\ flow \tag{8}$$

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.

$$\left[\frac{Product\ Price_p * Product\ mass\ flow_p}{\sum_{All\ products} Product\ Price * Product\ Mass\ flow}\right]_{base\ case} = \left[\frac{Product\ Price_p * Product\ mass\ flow_p}{\sum_{All\ products} Product\ Price * Product\ Mass\ flow}\right]_{ACS\ case} \tag{9}$$

3. Results and discussion

For the production of ethylene from CO_2 and biomass feedstocks, multiple technologies at different TRL were identified (see for example in Figure 2 the overview of CO_2-based routes*)*.

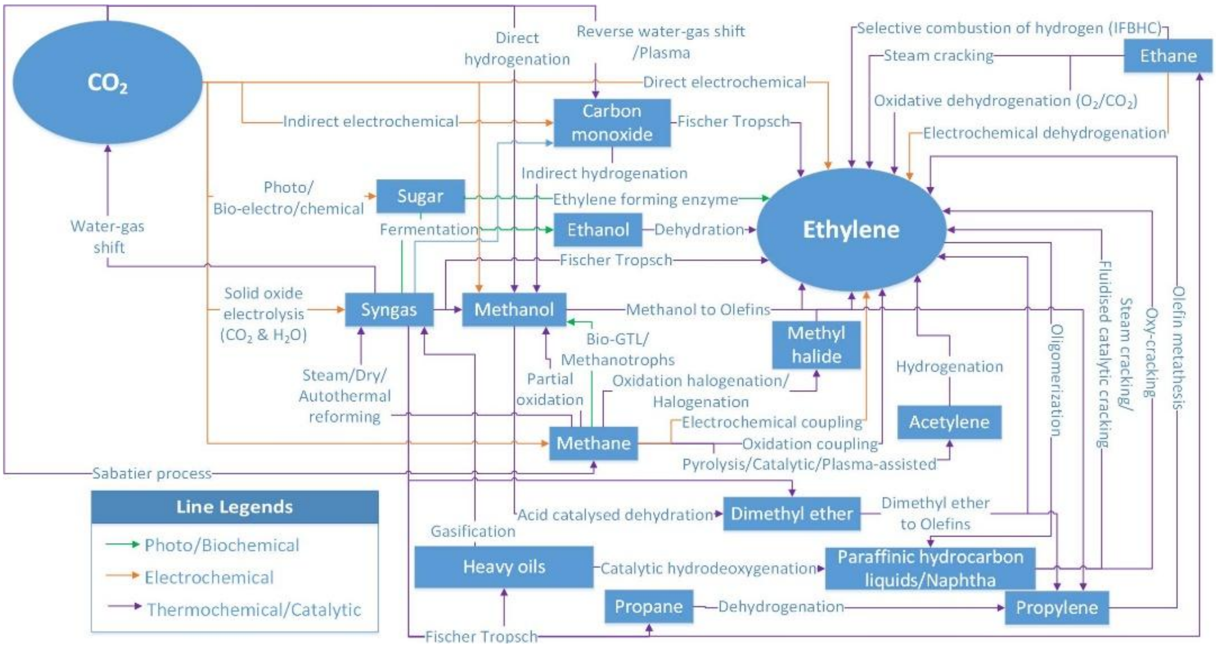

Figure 2: CO_2-based process routes for ethylene production

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 CO_2–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 H_2 for complete conversion of carbon in biomass. Hence, carbon is not fully utilised 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 CO_2 feedstocks respectively were: Biomass steam gasification (BSG) with Fischer-Tropsch (FT) process and direct electrochemical reduction (DER) of CO_2 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 chapter, only downstream plant impacts are studied using the preliminary results. The defossilisation 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 defossilisation 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 defossilisation strategies. The value chain carbon utilisation 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 defossilisation 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.[63] 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 defossilisation.

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 CO_2 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 defossilisation 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 defossilisation of one value chain can effect multiple value chains due to system interdependencies.

Th methodology based on stage-gate concept developed in this chapter will be used to further evaluate the impact of hydrogen origin on technology screening.

3. Why hydrogen origin matters for the screening of alternative carbon based technologies

Chapter specific nomenclature & symbols

Nomenclature

ACS	Alternative carbon source
ATR	Autothermal reformer
BF	Biomass fermentation
BG	Biogas production
Bio-GLT	Biogas to liquid
BN	Biochemical & endothermic
BOG	Biomass oxygen gasification
BSG	Biomass steam gasification
BX	Biochemical & exothermic
C2E	Carbon dioxide to ethylene
C2M	Carbon dioxide to methanol
CCS	Carbon capture and storage
CCUS	Carbon capture, utilisation and storage
CM2E	Carbon monoxide to ethylene
CN	Catalytic & endothermic
CUE	Carbon utilisation efficiency
CX	Catalytic & exothermic
DER	Direct electrochemical reduction
EIA	Environmental impact assessment
EL	Electrochemical
EN	Electricity need
ETO	Ethanol to olefin
f	Carbon and hydrogen origin feedstocks
FT	Fischer Tropsch
HI	Hydrogen import
HN	Heat need
HP	Heat production
IFBHC	Integrated fluidised bed hydrogen combustion
LCA	Life cycle analysis
MCDA	Multi-criteria decision analysis
MEA	Methyl ether amine
MTO	Methanol to olefins
PHTP	Plastic high temperature pyrolysis
PLTP	Plastic low temperature pyrolysis
POG	Plastic oxygen gasification
POSC	Pyrolysis oil steam cracking
PSG	Plastic steam gasification
RA	Risk analysis
SMR	Steam methane reformer
TEA	Techno-economic assessment
TN	Thermochemical & endothermic
TOPSIS	Technique of order preference similarity to the ideal solution
TRL	Technology readiness level
TX	Thermochemical & exothermic
WE	Water electrolysis
WGS	Water gas shift

Symbols

ΔG_r^0	Standard Gibbs free energy change of reaction
ΔH_r^0	Standard heat of reaction

Abstract

With the need for defossilising the petrochemical sector, a large number of options that use alternative carbon sources (ACS) like CO_2, biomass, and waste plastic are being developed. For instance, for producing ethylene, more than seventy different ACS-based process routes were identified in the literature. The selection of promising routes often involves the use of short-cut screening methodologies that compare options in terms of e.g., mass or energy requirements. To date, shortcut methodologies have overlooked the potential impact of assumptions regarding hydrogen origin in technology screening. This study addresses this gap by exploring the relevance of hydrogen origin when screening ACS-based ethylene production technologies. We examine four types of hydrogen origins: process hydrogen, green hydrogen, blue hydrogen and hydrogen import with assessment indicators carbon utilisation efficiency, electricity need, heat need and heat production. The results show that assumptions regarding hydrogen origin have a significant impact on the ranking of technologies.

1. Introduction

The petrochemical industry has relied for decades on the oil and gas sector as the primary source of raw materials. Developments in modern chemistry and the need for defossilising the petrochemical sector, have triggered an interest for developing alternative feedstocks and new process routes.[2] This opens many possibilities, including direct (one-step) or indirect (multi-step) routes to synthesise a chemical. For instance, to produce ethylene which is globally the largest volume industrially produced chemical;[64], over seventy different (direct and indirect) process routes have been identified in the literature[2,65–76] that use alternative carbon sources (ACS) like CO_2, biomass, and waste plastic (see Figure 1). The routes are at different levels of development and many of these routes will not be further developed and implemented due to, for instance, time and resource constrains or feasibility at large scale.

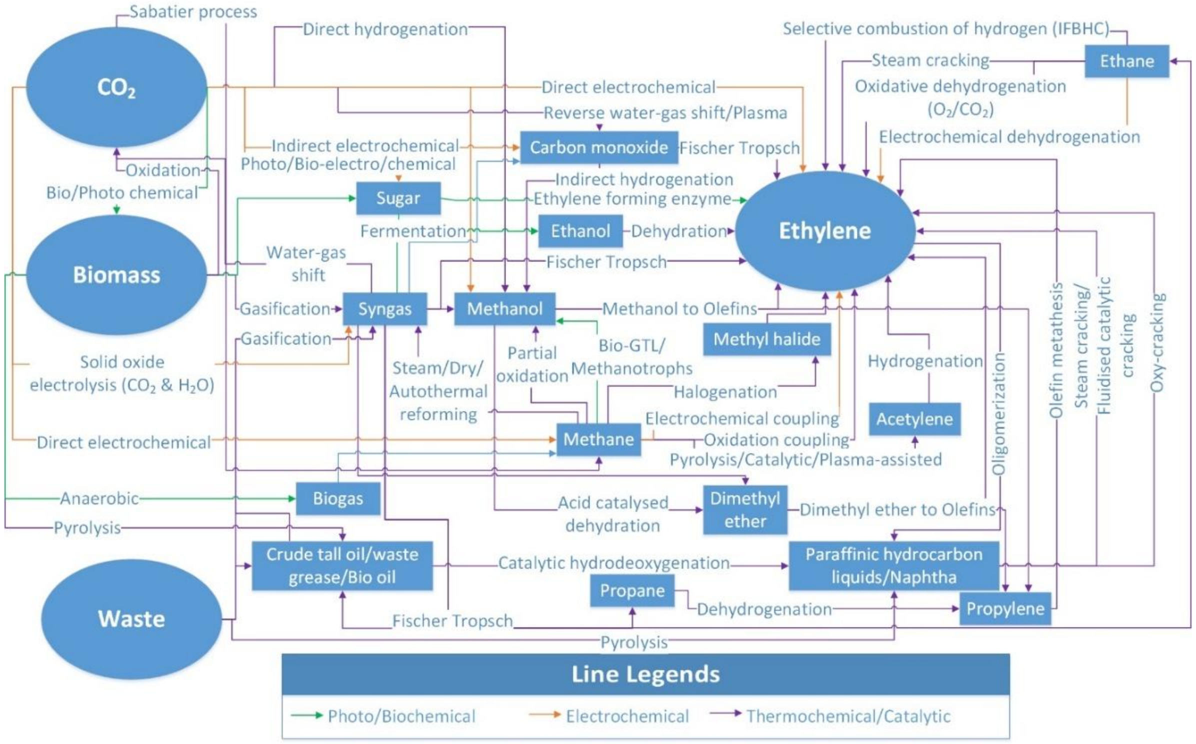

Figure 1: Possible pathways to produce ethylene from ACS feedstocks at different TRL. (Abbreviations: Bio-GTL: Biogas to liquid; IFBHC: Integrated Fluidised Bed Hydrogen Combustion).

As part of their R&D portfolio, universities, technology developers and companies perform technology screenings to select and further invest in those that appear more promising. The selection of a feedstock and the corresponding process route in the chemical industry is driven by considerations on (i) feedstock availability and cost; (ii) expenditures (capital & operational); (iii) product and by-product demand; (iv) environmental regulations; (v) production reliability, and (vi) safety.[2,26] Several multi-criteria decision-making methodologies encompassing insights from environmental impact assessment (EIA), risk analysis (RA), life cycle analysis (LCA) and/or techno-economic analysis (TEA) are often used for decision support.[9] Such assessments can be applied at an early conceptual design stage to support the development of R&D portfolios.[26] A key limitation is, however, that these approaches are time and data-intensive.

Alternatively, short-cut screening methods, which combine multi-criteria decision analysis with data from heuristics, ideal reactions, and/or short-cut models, are used to minimise the time and information needs, especially for comparing technologies at different technology readiness levels

(TRL).[26] For example, Sugiyama et al., [26] used a stage-gate approach[77] to propose a short-cut method, in which potential processes were shortlisted based on different selection criteria at the various stages. This method has the advantage that the required amount of information increases only for those technologies that advance to subsequent stages[26]. Zheng et al.,[18] proposed to use the Gibbs free energy of the involved reactions as a screening criterion, in addition to cost and material flow indicators. Othman et al.,[29] Patel et al.,[30] Posada et al.,[33] Moncada et al.,[31] and Warnasooriya et al.,[32] used multi-criteria decision analysis (MCDA) with technical, economic, environmental, social and safety indicators to screen early-stage biobased process routes. They used normalised scales, weight factors and global indexes to rank the technologies. The screening approach proposed by Patel et al[30] and Moncada et al[31] also included a literature review, interviews and short-cut modelling to collect information on specific parameters, to be used as input data in their energy and material indicator calculation. Santibanez-Aguilar et al.,[78] proposed using multi-objective optimisation for technology section, i.e. maximise profit and minimise environmental impact. In their study, they used mass and cost data collected from literature. Otto et al.,[16] screened 123 potential CO_2 utilisation pathways using 3 criteria: specific mass flow, CO_2 avoidance potential and economic value. While Pacheco et al.,[19] screened CO_2 utilisation pathways using as criteria TRL, product price, product demand, CO_2 utilisation potential, enthalpy and Gibbs free energy. Cui et al[20] used the TOPSIS (Technique of order preference similarity to the ideal solution) method to rank CO_2-based technologies using the techno-economic and environmental criteria: enthalpy, Gibbs energy, TRL, return on investment, market value and atomic efficiency calculated from literature data and information from short-cut process modelling. In Chapter 2,[79] we used the stage-gate approach based on the information from number of reaction steps, standard heat of reaction, standard Gibbs energy change, waste production, raw material prices and product prices to screen technologies for ethylene production. A stage-gate approach is used in this study rather than other multi-criteria decision making techniques like TOPSIS as it does not require weights and uses a cut-off (gate) based step-wise evaluation in which technologies are compared with each other for a particular criteria at each stage. This approach provides a robust ranking that avoids subjective scoring.

In the short-cut screening studies discussed above, the impact of underlying assumptions regarding hydrogen origin is not assessed. Hydrogen is generally assumed to be available for use as any other commodity. For instance, Otto et al[16], Chauvy et al[17], Pacheco et al[19] and Cui et al[20] assumed green hydrogen in their assessment, available at the system boundary, thereby disregarding any energy penalties related to hydrogen production in their analysis. Furthermore, in most studies, only one type of hydrogen source is generally considered even though hydrogen can be sourced from fossil or alternative sources through electrochemical, thermochemical or biochemical pathways (see Table 1). [80]

Table 1: Compilation of different hydrogen production routes.. (Abbreviations: CCUS- carbon capture, utilisation & storage)

Different hydrogen feedstocks		**Hydrogen types/colours**	**Examples of hydrogen production technologies**
Fossil based	Natural gas (CH_4)	- Grey hydrogen (reforming without CCUS) - Blue hydrogen (reforming with CCUS) - Turquoise hydrogen (pyrolysis)	Steam reforming, partial oxidation, dry reforming, pyrolysis
	Hydrocarbon $(-C_xH_y-)_n$	- Hydrogen from hydrocarbons - Hydrogen as byproduct of industrial processes	Dehydrogenation, cracking, aromatisation, reforming, partial oxidation, pyrolysis
	Coal (-C-)	- Brown hydrogen (from brown coal) - Black hydrogen (from black coal)	Steam-oxygen gasification

Alternative	Water (H_2O)	- Green hydrogen (using renewable energy) - Pink hydrogen (using nuclear energy) - Yellow hydrogen (using grid electricity) - White hydrogen (naturally occurring) - Hydrogen molecule/ion from redox reactions	Electrolysis, ionisation, thermolysis, radiolysis, geochemical, metal oxidation, water-gas shift
	Biomass/Plastic $(-C_xH_yO_z-)_n$	- Hydrogen from biomass - Hydrogen from plastic - Bio-hydrogen (bio-chemically produced)	Steam gasification, oxygen gasification, pyrolysis, cracking, photochemical, biochemical

Literature has, however, shown that the performance of an ACS-based process can vary depending on the hydrogen source and this has been substantiated in TEA and LCA studies. For example, Nabil et al.,[81] conducted a comparative cradle-to-gate LCA, to study the direct and indirect electrochemical reduction of CO_2 to ethylene among other chemicals. When comparing a direct electrochemical reduction and an indirect CO_2 hydrogenation route to ethylene, the direct route had a lower GHG emission (2.94 kg $CO_{2\text{-eq}}$/kg ethylene) than the indirect route (3.5 kg $CO_{2\text{-eq}}$/kg ethylene) due to the higher energy need of the indirect route (mostly due to hydrogen production). Hence, even though both technologies were electrochemical in nature, the hydrogen origin impacted their energy and environmental performance. For biomass feedstock, AlNouss et al.,[82] through a comparative TEA of syngas production (or hydrogen production) showed that the choice of technology impacted the overall methanol production performance due to the material and energy performance difference in hydrogen production from steam and oxygen gasification technologies,. Similarly, conclusions can be drawn from Ray et al.,[83] through a comparative assessment of oxygen gasification (i.e., hydrogen production through the syngas route) and pyrolysis (i.e., hydrogen production through the depolymerisation route) from waste plastic. They showed that the hydrogen origin had a significant impact on the utility needs, as pyrolysis process required 1390 kWh heat/tonne of waste plastic for depolymerisation, while oxygen gasification required no heating utility but needed 115 kWh electricity/tonne of waste plastic for oxygen generation. Thus, these studies show that the hydrogen origin had a significant impact on material, energy and environmental performance of ACS-based technologies; and this impact has generally not been taken into account in short-cut screening methodologies. This study addresses this knowledge gap and it aims to explore the significance of hydrogen origin when using short-cut screening of technologies at early stage of development.

2. Methodology

To explore the potential impact of hydrogen origin in technology screening, the ACS-based ethylene production was selected in the study, as ethylene is the highest volume produced petrochemical in the world, currently mainly produced from naphtha or ethane[64]. To study the relevance of hydrogen origin when screening ACS-based process routes, two system boundaries were considered: Boundary-1 (ACS-based process only) and boundary-2 (ACS-based process and an external hydrogen source). The ACS-based processes were classified based on the hydrogen origin as: processes with inherent hydrogen production (i.e. routes that produce hydrogen as part of the chemical reactions during ethylene production, referred here as "internal production") and processes that require external (low carbon) hydrogen supply due to insufficient internal hydrogen production, the so called "external production". The technologies were assessed for ideal reactions at standard temperature and pressure conditions using material and energy indicators for the two boundaries using input (raw-materials and energy) and output (products, waste and energy) streams. Thus, this chapter uses an input-output based analysis and does not include other techno-economic or environmental assessment like CAPEX analysis or LCA analysis. This simplified methodology is used, because when assessing a large number of technologies (as in this case more than 70 technologies), it would be too resource and time intensive to study all the technologies at the same level of detail. Hence, such simplified pre-screening methodologies helps to identify a handful of promising routes which can be used for detailed TEA and LCA studies. Further details of the methodology used in this chapter are provided below.

2.1 Hydrogen origin and system boundaries

The hydrogen origins considered in this work are summarised in Table 2. The ACS-based processes with inherent hydrogen production include, for example, the direct electrochemical reduction of the CO_2-H_2O mixture or biomass steam gasification. Processes that require external production are for instance, biomass steam gasification1 or plastic oxygen gasification1. The external hydrogen required for such processes was assumed to be supplied by either on-site green (water electrolysis) or on-site blue hydrogen (steam methane reforming with carbon capture & storage) technologies. In this study, water electrolysis technologies like proton exchange membrane or alkaline electrolysis and low temperature or high temperature electrolysis were not differentiated, as ideal stoichiometric reactions and thermodynamic state function at standard temperature and pressure conditions (1 bar and 25 °C) were used for the assessment.

Table 2: Different hydrogen origins considered in this study for the production of ethylene. (Detailed tables provided in supplementary information Table S1 & Table S2)

Hydrogen origins	For CO_2	For Biomass	For Waste plastic
ACS-based process with inherent hydrogen production (internal production)	- Electrochemical reduction of CO_2-H_2O mixture	- Biomass steam gasification (BSG) - Biomass oxygen gasification (BOG) - Biomass steam gasification (BSG) with water gas shift (WGS) - Biomass oxygen gasification (BOG) with water gas shift (WGS) - Biomass fermentation (BF) - Anaerobic digestion or biogas production (BG)	- Plastic steam gasification (PSG) - Plastic oxygen gasification (POG) - Plastic oxygen gasification (POG) with water gas shift (WGS) - Plastic low temperature pyrolysis (PLTP) - Plastic high temperature pyrolysis (PHTP)
External low carbon hydrogen source (external production)	- Water electrolysis (WE) - Steam methane reforming (SMR) with carbon capture & storage (CCS)		

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[1] These process produces a CO to H_2 ratio of 1:1 while downstream synthesis of ethylene requires a CO to H_2 ratio of 1:2 and thus requires either syngas conditioning or an external hydrogen supply

In the case of CO_2 used as feedstock, only electrochemical CO_2-H_2O mixture reduction-based routes inherently produce hydrogen while biomass and plastic used as feedstocks can provide both carbon and hydrogen. Therefore, routes that use CO_2 as feedstock in other indirect electrochemical or thermal ACS-based processes require an external hydrogen source for ethylene production. For the biomass and plastic ACS-based routes, due to the inherent hydrogen and carbon content of these feedstocks (as given in supplementary information section Table S3), technologies like gasification, biochemical or pyrolysis can produce internal hydrogen. However, even though they have inherent hydrogen production, some routes require an external hydrogen supply due to the insufficient hydrogen to carbon ratio to synthesise ethylene, like the technologies BSG, BOG and POG without WGS.

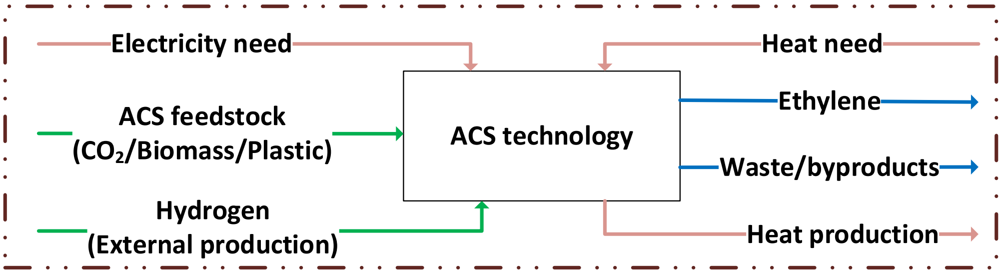

Figure 2: Boundary-1 (ACS process only case) considered in this study to assess the relevance of hydrogen origin for technology screening of ACS feedstocks.

As indicated previously, two system boundaries were considered in this study, as shown in Figure 2 and Figure 3. Within boundary-1, only the ACS-based process was included and any additional or external hydrogen need was considered as an input stream, while in boundary-2, both the ACS-based process and the external hydrogen production, were included.

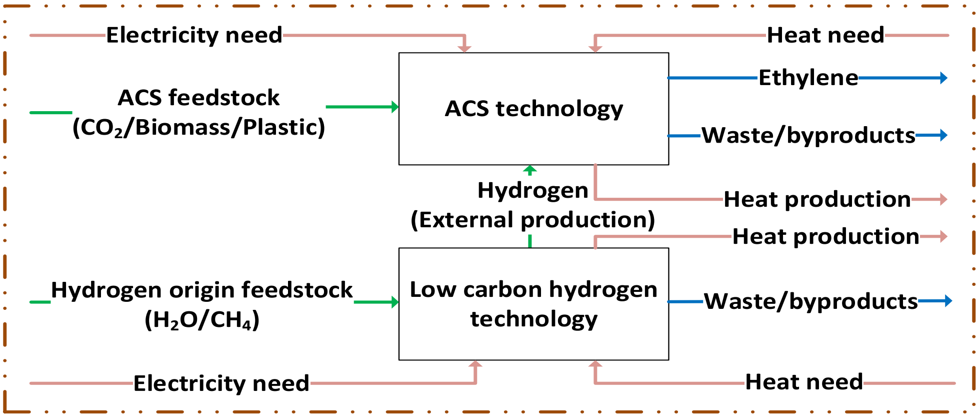

Figure 3: Boundary-2 (ACS process + external hydrogen source case) considered in this study to assess the relevance of hydrogen origin for technology screening of ACS feedstocks.

Electricity and heat need for the ACS-based process were assumed to be inputs. The impact on technology selection due to the different energy sources was not part of the assessment in this study.

2.2 Technology screening and multi-criteria assessment

The screening methodology used in this chapter was based on the stage-gate approach used in Chapter 2,[79] considering boundaries 1 and 2. In the stage-gate approach, criteria at different stages of selection (gates) were used to identify promising routes for the conversion of ACS feedstock into ethylene. Herein, the term “promising” in the context of this chapter refers to the comparative performance based on material and energy indicators, while the term “gate” refers to the indicator threshold value required to pass to the next stage. The screening methodology considers three stages and gates, as shown in Table 3. The indicators used were: TRL, number of reaction steps, and a combination of carbon utilisation efficiency (CUE)[79], heat production (HP)[79], heat need (HN)[79] and electricity need (EN)[79] (see Table 3 and supplementary information section S3). In stage-3, the energy indicators (HP, HN and EN) are used along with material efficiency indicator (CUE); as processes can show good energy performance by compromising material efficiencies and to take this into account the indicators are assessed together.[79]

Table 3: Selection criteria used for screening technologies (where: ΔH_r^0=Standard heat of reaction, ΔG_r^0 =Standard Gibbs free energy change, BX= Biochemical & exothermic reaction, TX= Thermochemical & exothermic reaction, CX= Catalytic & exothermic reaction, BN= Biochemical & endothermic reaction, TN= Thermochemical & endothermic reaction, CN= Catalytic & endothermic reaction, EL= Electrochemical reaction, f=carbon & hydrogen origin feedstocks, CUE= Carbon utilisation efficiency, HP= Heat production, HN= Heat need, EN= Electricity need)

Stages	Indicator	Gate
Stage-1	TRL scale[84]	TRL > 3
Stage-2	Number of reaction steps= Number of ideal stoichiometric reactions	Number of reaction steps <4
Stage-3	$Carbon\ utilisation\ efficiency\ (CUE) = \frac{Moles\ of\ carbon\ atom\ in\ \text{Ethylene}}{\sum_{n=1}^{n=f} Moles\ of\ carbon\ atom\ in\ feedstock(n)}$ $Heat\ production\ (HP) = \sum_{i=1}^{i=BX} \Delta H_{r(i)}^0 + \sum_{j=1}^{j=TX} \Delta H_{r(j)}^0 + \sum_{k=1}^{k=CX} \Delta H_{r(k)}^0$ $Heat\ need\ (HN) = \sum_{i=1}^{i=BN} \Delta H_{r(i)}^0 + \sum_{j=1}^{j=TN} \Delta H_{r(j)}^0 + \sum_{k=1}^{k=CN} \Delta H_{r(k)}^0$ $Electricity\ need\ (EN) = \sum_{i=1}^{i=EL} \Delta \mathrm{G}_{r(i)}^0$	Sorted based on highest CUE, lowest EN, lowest HN, highest HP, in this order, to select one route from each hydrogen origin category

The material and energy indicators were calculated based on ideal reactions at standard temperature & pressure conditions (1 bar and 25 °C) using thermodynamic state functions as shown in Table 3. The phase (solid, liquid, gas or vapor) of the input and output components used was the one on their respective state at standard temperature and pressure conditions. The term ideal reaction in this chapter means ideal stoichiometric reactions which does not take into account faraday efficiency, selectivity, side reactions and reaction equilibrium; to produce one mole of ethylene. The energy indicators (EN, HN and HP) correspond to the energy production or needs associated with the chemical reactions only; other energy needs or losses due to voltage overpotential, heat transfer losses, process heating, process cooling, feed pretreatment (like biomass drying, production of O_2 & CO_2), product purification, pressurisation and material transport are not taken into account. Hence, the results of this assessment provide the most optimistic case for the technologies. As the analysis in this study is for the production of one mole of ethylene, other aspects like feedstock availability and energy availability are also not considered.

Based on literature[2,65–76], we identified 70 pathways at TRL 4-9 for the production of ethylene from CO_2, biomass and waste plastic, i.e.; 24 pathways for CO_2, 27 pathways for biomass and 19 pathways for waste plastic (as given in the supplementary information Table S4, Table S6 and Table S8). Considering the three ACS feedstocks (CO_2, biomass and waste plastic), from a total of 19 hydrogen origin categories (i.e. 11 internal production-based, 2 external production-based, and 6 a combination of internal and external based as shown in Appendix A Table A1, Table A2 and Table A3), one technology from each hydrogen origin was selected for the multi-criteria assessment to study the relevance of hydrogen origin on technology screening.

In the multi-criteria assessment covering different ACS feedstocks and hydrogen origins, the selected technological pathways from each hydrogen origin category were compared using the stage-3 indicators (CUE, EN, HN and HP). In order to be able to pinpoint promising processes, the indicators carbon utilisation versus electricity or heat needs and carbon utilisation versus heat production were plotted in two-dimensional or bi-objective graphs. The solutions that configured the pareto fronts in the bi-objective graphs for boundaries 1 and 2 were then analysed and discussed. The effect of including the downstream product separation on technology selection could not be performed in this study, as (1) because of the simplified assumption of ideal reactions, no byproducts or impurities were considered and (2) the simplified thermodynamic methodology could not analyse separation processes like distillation. To understand whether not including CO_2 removal step during syngas or hydrogen cleaning had an impact on technology screening, a methyl ether amine (MEA) based carbon capture reaction was used for all the stage-3 selected routes which required CO_2 removal process step. The energy required

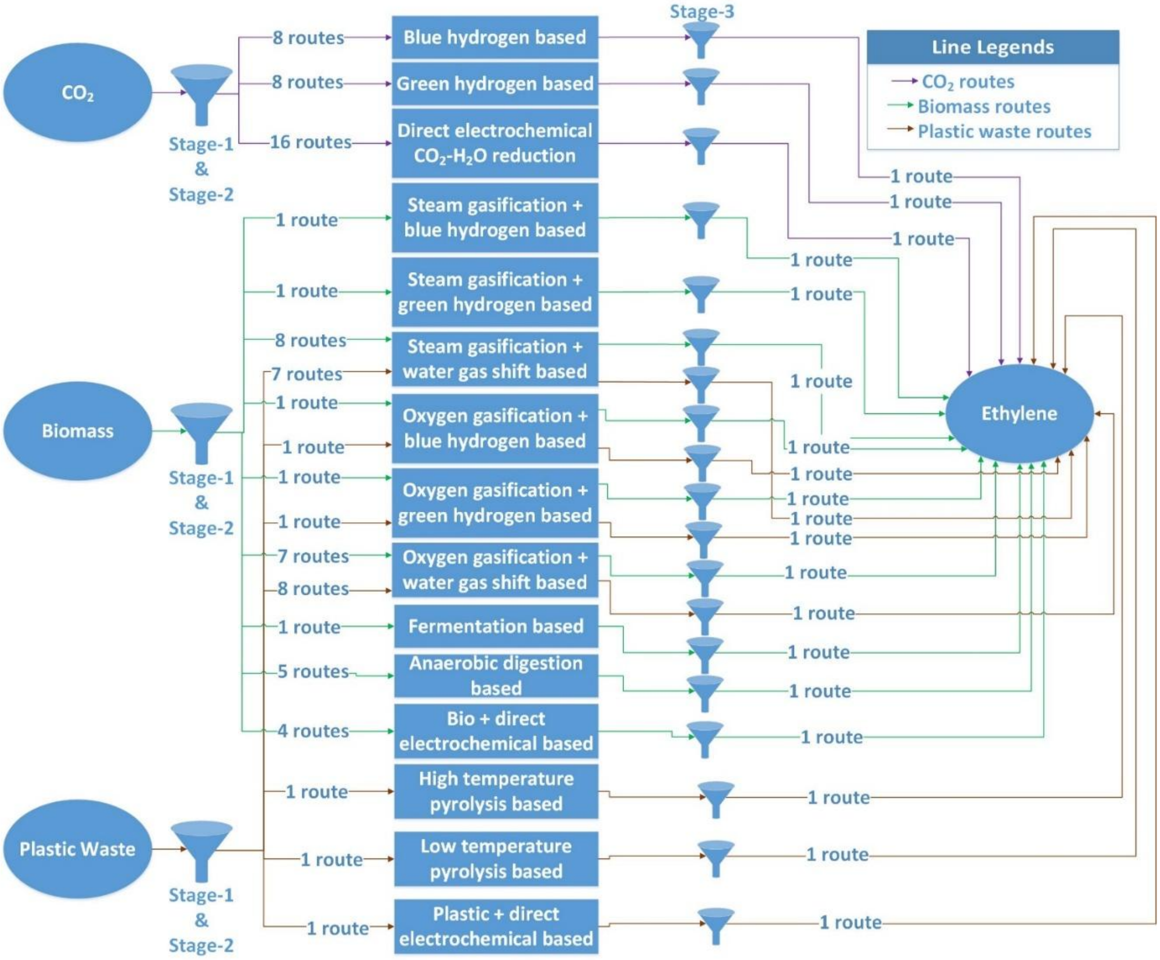

Figure 4: ACS technology screening schematic with hydrogen origin categorisation in boundary-2

for the MEA based CO_2 removal process was calculated in a Gibbs reactor at standard temperature & pressure conditions in Aspen plus and was used in the multi-criteria assessment. MEA was selected as the solvent in this study as it is the most widely used CO_2 absorbent due to its high selectivity, quick reaction and low cost.[85]

3. Results and discussion

The technologies are categorised based on the hydrogen origin (as shown in Figure 4) during the technology selection and using the screening methodology (Stage-1, 2 & 3), one technology from each hydrogen origin is selected for the final assessment. In boundary-1, blue and green hydrogen are not distinguished as this case considers the reference case where the source of hydrogen is not considered, while in boundary-2, two possibilities are considered for external hydrogen need.

3.1 Boundary-1 (considering ACS-based process only)

For the use of CO_2 as feedstock, out of the 24 pathways, 16 routes are CO_2-H_2O electrochemical processes with inherent hydrogen production and 8 routes have external hydrogen needs (see Appendix A). Table 4 shows the result of the assessment considering boundary-1. From the two hydrogen origin categories the selected CO_2-based routes are: CO_2 hydrogenation to methanol (C2M) with methanol to olefin (MTO) and direct electrochemical reduction (DER) of CO_2-H_2O to ethylene (C2E).

Ideally, from the 12 moles of H_2O (or 12 moles of H+ ions) required to produce ethylene from CO_2, about 67% of hydrogen is used to remove the oxygen from the CO_2 (Table 4). Because of this high hydrogen need, the direct electrochemical reduction process requires 1332 kJ electrical energy to synthesise 1 mole of ethylene. Considering boundary-1, all the indirect CO_2 hydrogenation-based routes are exothermic and there is theoretically no reaction energy need in these routes.

Table 4: Selected technologies from different hydrogen origins (internal and external) for CO_2 feedstock considering boundary-1. (Abbreviations: DER- Direct electrochemical reduction, C2E- CO_2 to ethylene, HI- Hydrogen import, C2M- CO_2 to methanol, MTO- Methanol to olefin). Note: The negative sign refers to energy production and the positive sign refers to energy need.

Routes	Ideal stoichiometric reactions	CUE	kJ/mol ethylene		
			EN	HN	HP
HI + C2M + MTO	$2\,CO_2 + 6\,H_2(100\%\ import) \rightarrow 2CH_3OH + 2\,H_2O$ $2CH_3OH \rightarrow C_2H_4 + 2\,H_2O$	100%	0	0	-304
DER (C2E)	$Cathode: 2\,CO_2 + 12\,H_2O + 12\,e^- \rightarrow C_2H_4 + 4\,H_2O + 12\,OH^-$ $Anode: 12\,OH^- \rightarrow 6\,H_2O + 3\,O_2 + 12\,e^-$	100%	1332	0	0

For ACS-ethylene routes that use biomass as feedstock, out of the 27 pathways, 6 routes are biochemical, 8 are steam gasification-based, 7 are oxygen gasification-based, 4 are electrochemical-based and 2 are external hydrogen supply-based (see Appendix A). Thus, within boundary-1, there are seven hydrogen origin possibilities, namely: steam gasification with water gas shift, oxygen gasification with water gas shift, fermentation, anaerobic digestion, biogenic CO_2-H_2O based electrochemical, steam gasification with hydrogen import and oxygen gasification with hydrogen import. Most biomass-based processes do not require external hydrogen because biomass has a molar hydrogen to carbon ratio between 1.2-2[86]. There are different needs in the amount of external hydrogen, for instance, biomass steam gasification only requires 2 moles of external hydrogen (i.e., 50% hydrogen import) due to its internal hydrogen production, while biomass oxygen gasification requires 4 moles of external hydrogen (i.e., 100% hydrogen import) in the 100% CUE case. With WGS reaction both biomass steam and oxygen gasification can also inherently produce hydrogen at other CUE cases (see Table 5). Based on the results shown in Table 5, the selected technologies for the different hydrogen origins are: biomass steam gasification (BSG) with water gas shift (WGS) and Fischer-Tropsch (FT), biomass oxygen gasification (BOG) with WGS and FT, BSG with hydrogen import (HI) and FT process, BOG with HI and FT process, biogas production (BG) with autothermal reforming (ATR) and FT process, biomass fermentation (BF) to ethanol with ethanol to olefin (ETO) and BF with ETO and DER (C2E).

In terms of energy needs, during the hydrogen production process step, the technologies like biomass oxygen gasification process (BOG), biomass fermentation (BF) and biogas production (BG) are exothermic (see Table 5) while biomass steam gasification requires heat in net terms, due to the exothermic and endothermic nature of the reactions. In all the selected routes, the ethylene formation reaction, i.e., FT reaction, is exothermic except in the case of the ETO process. For the ETO-based process a higher CUE could be achieved by converting the excess CO_2 formed during the fermentation process to ethylene by the direct electrochemical process. The CUE values indicates that the high exothermicity in BOG with WGS and FT route compared to BOG with HI and FT route is achieved by compromising feedstock carbon, as most of the feedstock carbon is converted to CO_2 by the exothermic water-gas-shift reaction to produce hydrogen. Because of these differences in internal hydrogen production through carbon usage, biomass-based technologies show a wide range in the carbon utilisation efficiency (33% to 100% as provided in the supplementary information Table S6).

Table 5: Selected technologies from different hydrogen origins (internal and external) for biomass feedstock considering boundary-1. (Abbreviations: BSG- Biomass steam gasification, FT- Fischer Tropsch, BOG- Biomass oxygen gasification, BF- Biomass fermentation, BG- Biogas production, ATR- Autothermal reforming, ETO- Ethanol to olefin, HI- Hydrogen import, WGS- Water gas shift, DER- Direct electrochemical reduction, C2E- CO_2 to Ethylene). Note: The negative sign refers to energy production and the positive sign refers to energy need.

Routes	**Ideal stoichiometric reactions**	**CUE**	**kJ/mol ethylene**		
			EN	**HN**	**HP**
HI + BOG + FT	$2/6\ C_6H_{10}O_5 + O_2 \rightarrow 2\ CO + 10/6\ H_2O$ $2\ CO + 4\ H_2 (100\%\ import) \rightarrow C_2H_4 + 2\ H_2O$	100%	0	0	-727
HI + BSG + FT	$2/6\ C_6H_{10}O_5 + 2\ H_2O \rightarrow 2\ CO + 2\ H_2 + 10/6\ H_2O$ $2\ CO + 4\ H_2 (50\%\ import) \rightarrow C_2H_4 + 2\ H_2O$	100%	0	215	-371
BF + ETO + DER (C2E)	$1/6\ C_{12}H_{22}O_{11} + 1/6\ H_2O \rightarrow 2/3\ C_2H_5OH + 2/3\ CO_2$ $2/3\ C_2H_5OH \rightarrow 2/3\ C_2H_4 + 2/3\ H_2O$ $Cathode: 2/3\ CO_2 + 4\ H_2O + 4\ e^- \rightarrow 1/3\ C_2H_4 + 4/3\ H_2O + 4\ OH^-$ $Anode: 4\ OH^- \rightarrow 2\ H_2O + O_2 + 4\ e^-$	100%	444	59	-65
BSG + WGS + FT	$0.5\ C_6H_{10}O_5 + 3\ H_2O \rightarrow 2\ CO + CO_2 + 4\ H_2 + 1.5\ H_2O$ $2\ CO + 4\ H_2 \rightarrow C_2H_4 + 2\ H_2O$	67%	0	282	-364
BF + ETO	$0.25\ C_{12}H_{22}O_{11} + 0.25\ H_2O \rightarrow C_2H_5OH + CO_2$ $C_2H_5OH \rightarrow C_2H_4 + H_2O$	67%	0	88	-98
BG + ATR + FT	$1/3\ C_{12}H_{22}O_{11} + 1/3\ H_2O \rightarrow 2\ CH_4 + 2\ CO_2$ $2\ CH_4 + O_2 \rightarrow 2\ CO + 4\ H_2$ $2\ CO + 4\ H_2 \rightarrow C_2H_4 + 2\ H_2O$	50%	0	0	-540
BOG + WGS + FT	$C_6H_{10}O_5 + 3\ O_2 \rightarrow 2\ CO + 4\ CO_2 + 4\ H_2 + H_2O$ $2\ CO + 4\ H_2 \rightarrow C_2H_4 + 2\ H_2O$	33%	0	0	-1575

For ACS-based routes to ethylene that use waste plastic as carbon feedstock, out of the 19 pathways, 2 routes are pyrolysis-based, 7 are steam gasification-based, 8 are oxygen gasification-based, 1 is electrochemical-based and 1 is external hydrogen supply-based (see Appendix A). Only plastic oxygen gasification without WGS need external hydrogen (see Table 6). Waste plastic-based technologies like steam gasification and pyrolysis are endothermic, as thermal energy is needed to break down the polymer into syngas or lower-weight hydrocarbons. Considering boundary-1, there were six hydrogen origin possibilities for waste plastic feedstock with routes based on gasification and pyrolysis: plastic oxygen gasification (POG) with hydrogen import (HI) and FT, POG with WGS and FT, POG with DER (CO to ethylene) and FT, plastic steam gasification (PSG) and FT, plastic high temperature pyrolysis (PHTP) and plastic low temperature pyrolysis (PLTP) with pyrolysis oil steam cracking (POSC).

The CUE values show that, similar to biomass oxygen gasification, technologies that are based on plastic oxygen gasification with a WGS reaction showed better energy performance due to the exothermic nature of the WGS reaction and the internal hydrogen production (Table 6). The CUE of the plastic oxygen gasification route could be improved by hydrogen import or through direct electrochemical conversion of the excess CO formed during the gasification process. The plastic oxygen gasification-based route with hydrogen import required 2 moles of external H_2 (i.e., 50% of required hydrogen). Among waste plastic-based technologies, the plastic oxygen gasification with hydrogen import and Fischer Tropsch performs better in terms of material and energy indicators as it has, ideally, higher CUE with no external energy needs.

Table 6: Selected technologies from different hydrogen origins (internal and external) for plastic feedstock considering boundary-1. (Abbreviations: PHTP- Plastic high temperature pyrolysis, PLTP- Plastic low temperature pyrolysis, POSC- Pyrolysis oil steam cracking, PSG- Plastic steam gasification, FT- Fischer Tropsch, POG- Plastic oxygen gasification, HI- Hydrogen import, WGS- Water gas shift, DER- Direct electrochemical reduction, CM2E- CO to Ethylene). Note: The negative sign refers to energy production and the positive sign refers to energy need.

Routes	**Ideal stoichiometric reactions**	**CUE**	**kJ/mol ethylene**		
			EN	**HN**	**HP**
HI + POG + FT	$Polyethylene\ (-C_2H_4-)_n + n\,O_2 \rightarrow 2n\,CO + 2n\,H_2$ $2n\,CO + 4n\,H_2(50\%\ import) \rightarrow n\,C_2H_4 + 2n\,H_2O$	100%	0	0	-466
PHTP	$Polyethylene\ (-C_2H_4-)_n \xrightarrow[Depolymerisation]{} n\,C_2H_4$	100%	0	106	0
PSG + FT	$Polyethylene\ (-C_2H_4-)_n + 2n\,H_2O \rightarrow 2n\,CO + 4n\,H_2$ $2n\,CO + 4n\,H_2 \rightarrow n\,C_2H_4 + 2n\,H_2O$	100%	0	404	-298
PLTP + POSC	$Polyethylene\ (-C_2H_4\ -)_{6n} \xrightarrow[Pyrolysis]{} Naphtha\ (n\,C_{12}H_{24})$ $Naphtha(C_{12}H_{24}) \xrightarrow[Cracking]{} 2\,H_2 + CH_4 + C_2H_4 + C_3H_6 + C_6H_6$	100%	0	402	0
POG + FT + DER (CM2E)	$Polyethylene\ (-C_2H_4-)_n + n\,O_2 \rightarrow 2n\,CO + 2n\,H_2$ $n\,CO + 2n\,H_2 \rightarrow 0.5\,n\,C_2H_4 + n\,H_2O$ $Cathode: CO + 2\,H_2O + 2\,e^- \rightarrow 0.5\,C_2H_4 + H_2O + 2\,OH^-$ $Anode: 2\,OH^- \rightarrow H_2O + 0.5\,O_2 + 2\,e^-$	100%	409	0	-317

POG + WGS + FT	$Polyethylene(-C_2H_4-)_{2n}$ $+3nO_2 \rightarrow 2n\ CO + 2n\ CO_2 + 4nH_2$ $2n\ CO + 4n\ H_2 \rightarrow n\ C_2H_4 + 2n\ H_2O$	50%	0	0	-1199

3.2 Boundary-2 (considering ACS-based process & external hydrogen source)

Table 7 shows the results of the assessment using boundary-2, for CO_2 feedstock. Three hydrogen origin possibilities for the reduction of CO_2 to ethylene were identified, i.e., direct electrochemical reduction of CO_2-H_2O, green hydrogen and blue hydrogen. The electricity need (EN) indicator shows that all CO_2 routes are endergonic, i.e. all CO_2 routes need electricity or heat for the reduction of CO_2, hydrogen production or both. Theoretically, the direct electrochemical route to ethylene has a slightly higher energy efficiency compared to the indirect routes, as it requires ~6% lower electricity than the indirect route. This is because even though both, the direct and indirect routes, require the same amount of hydrogen (12 H+ ions or 6 H_2 molecules), there are differences in the hydrogenation and oxygen removal processes. In the indirect process, the CO_2 hydrogenation is an exothermic thermochemical step (as shown in Table 7) while for the direct route, the hydrogenation process is part of the electrochemical hydrogen generation step. As the hydrogenation process is an exergonic process, the difference in how the hydrogenation occurs (i.e., thermochemical or electrochemical), results in higher theoretical energy needs for indirect routes. Similarly, a comparison of green and blue hydrogen-based routes shows that the hydrogen origin makes a substantially difference in the energy needs, as a SMR process requires 379 kJ (heat) while a water electrolysis-based process requires 1423 kJ (electricity).

Table 7: Selected technologies from different hydrogen origins (internal and external) for CO_2 feedstock considering boundary-2 (Abbreviations: DER- Direct electrochemical reduction, C2E- CO_2 to ethylene, WE-Water electrolysis (green hydrogen), C2M- CO_2 to methanol, MTO- Methanol to olefin, SMR- Steam methane reforming (blue hydrogen)). Note: The negative sign refers to energy production and the positive sign refers to energy need.

Routes	Ideal stoichiometric reactions	CUE	kJ/mol ethylene		
			EN	HN	HP
DER (C2E)	$Cathode: 2\ CO_2 + 12\ H_2O + 12\ e^-$ $\rightarrow C_2H_4 + 4\ H_2O + 12\ OH^-$ $Anode: 12\ OH^- \rightarrow 6\ H_2O + 3\ O_2 + 12\ e^-$	100%	1332	0	0
WE + C2M + MTO	$Cathode: 12\ H_2O + 12\ e^-$ $\rightarrow 6\ H_2 + 12\ OH^-$ $Anode: 12\ OH^- \rightarrow 6\ H_2O + 3\ O_2 + 12\ e^-$ $2\ CO_2 + 6\ H_2 \rightarrow 2CH_3OH$ $+ 2\ H_2O\ (Thermochemical)$ $2CH_3OH \rightarrow C_2H_4$ $+ 2\ H_2O\ (Thermochemical)$	100%	1423	0	-304
SMR + C2M + MTO	$1.5\ CH_4 + 3\ H_2O \rightarrow 6\ H_2 + 1.5\ CO_2$ $2\ CO_2 + 6\ H_2 \rightarrow 2CH_3OH + 2\ H_2O$ $2CH_3OH \rightarrow C_2H_4 + 2\ H_2O$	57%	0	379	-304

In this boundary, the origin of hydrogen did not impact the CUE for the CO_2-H_2O electrochemical and water electrolysis-based routes. In the case of blue hydrogen, when the CO_2 from the production of blue hydrogen is not directly utilised for the production of ethylene (e.g., it is directly emitted to the atmosphere), the CUE is 57%, i.e., the blue hydrogen-based route produces about 2.4 kg excess CO_2 per kg of ethylene produced, which results in a lower CUE than for the other cases. Thus, in the case of blue hydrogen, when the CO_2 from the production of blue hydrogen is not directly used for the production of ethylene, about 2.36 kg CO_2 were formed per kg of ethylene produced.

Table 8: Selected technologies from different hydrogen origins (internal and external) for biomass feedstock considering boundary-2 (Abbreviations: BSG- Biomass steam gasification, FT- Fischer Tropsch, BOG- Biomass oxygen gasification, WE- Water electrolysis (green hydrogen), SMR- Steam methane reforming (blue hydrogen), BF- Biomass fermentation, BG- Biogas production, ATR- Autothermal reformer, ETO- Ethanol to olefin, WGS- Water gas shift, DER- Direct electrochemical reduction, C2E- CO_2 to Ethylene). Note: The negative sign refers to energy production and the positive sign refers to energy need.

Routes	Ideal stoichiometric reactions	CUE	kJ/mol ethylene		
			EN	HN	HP
BF + ETO + DER (C2E)	$1/6\ C_{12}H_{22}O_{11} + 1/6\ H_2O \rightarrow 2/3\ C_2H_5OH + 2/3\ CO_2$ $2/3\ C_2H_5OH \rightarrow 2/3\ C_2H_4 + 2/3\ H_2O$ $Cathode: 2/3\ CO_2 + 4\ H_2O + 4\ e^- \rightarrow 1/3\ C_2H_4 + 4/3\ H_2O + 4\ OH^-$ $Anode: 4\ OH^- \rightarrow 2\ H_2O + O_2 + 4\ e^-$	100%	444	59	-65
WE + BSG + FT	$Cathode: 4\ H_2O + 4\ e^- \rightarrow 2\ H_2 + 4\ OH^-$ $Anode: 4\ OH^- \rightarrow 2\ H_2O + O_2 + 4\ e^-$ $2/6\ C_6H_{10}O_5 + 2\ H_2O \rightarrow 2\ CO + 2\ H_2 + 10/6\ H_2O$ $2\ CO + 4\ H_2 \rightarrow C_2H_4 + 2\ H_2O$	100%	474	215	-371
WE + BOG + FT	$Cathode: 8\ H_2O + 8\ e^- \rightarrow 4\ H_2 + 8\ OH^-$ $Anode: 8\ OH^- \rightarrow 4\ H_2O + 2\ O_2 + 8\ e^-$ $2/6\ C_6H_{10}O_5 + O_2 \rightarrow 2\ CO + 10/6\ H_2O$ $2\ CO + 4\ H_2 \rightarrow C_2H_4 + 2\ H_2O$	100%	949	0	-727
SMR + BSG + FT	$2/6\ C_6H_{10}O_5 + 2\ H_2O \rightarrow 2\ CO + 2\ H_2 + 10/6\ H_2O$ $0.5\ CH_4 + H_2O \rightarrow 2\ H_2 + 0.5\ CO_2$ $2\ CO + 4\ H_2 \rightarrow C_2H_4 + 2\ H_2O$	80%	0	342	-371
SMR + BOG + FT	$2/6\ C_6H_{10}O_5 + O_2 \rightarrow 2\ CO + 10/6\ H_2O$ $CH_4 + 2\ H_2O \rightarrow 4\ H_2 + CO_2$ $2\ CO + 4\ H_2 \rightarrow C_2H_4 + 2\ H_2O$	67%	0	253	-727
BSG + WGS + FT	$0.5\ C_6H_{10}O_5 + 3\ H_2O \rightarrow 2\ CO + CO_2 + 4\ H_2 + 1.5\ H_2O$ $2\ CO + 4\ H_2 \rightarrow C_2H_4 + 2\ H_2O$	67%	0	282	-364
BF + ETO	$0.25\ C_{12}H_{22}O_{11} + 0.25\ H_2O \rightarrow C_2H_5OH + CO_2$ $C_2H_5OH \rightarrow C_2H_4 + H_2O$	67%	0	88	-98
BG + ATR + FT	$1/3\ C_{12}H_{22}O_{11} + 1/3\ H_2O \rightarrow 2\ CH_4 + 2\ CO_2$ $2\ CH_4 + O_2 \rightarrow 2\ CO + 4\ H_2$ $2\ CO + 4\ H_2 \rightarrow C_2H_4 + 2\ H_2O$	50%	0	0	-540
BOG + WGS + FT	$C_6H_{10}O_5 + 3\ O_2 \rightarrow 2\ CO + 4\ CO_2 + 4\ H_2 + H_2O$ $2\ CO + 4\ H_2 \rightarrow C_2H_4 + 2\ H_2O$	33%	0	0	-1575

For the biomass process routes, there were nine different hydrogen origin possibilities using variations of gasification, electrolysis, SMR, anaerobic digestion and fermentation, as shown in Table

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[2] Only SMR reaction energy is shown and the carbon capture or product cleaning energy is not taken into account in this study

8. In the case of biomass, hydrogen could be inherently produced with the seven technologies, i.e.; steam gasification, oxygen gasification, steam gasification with WGS, oxygen gasification with WGS, anaerobic digestion, direct electrochemical and fermentation. For the two routes with water electrolysis-based hydrogen, the oxygen gasification-based route has significantly higher electricity needs than steam gasification (949 kJ vs 474 kJ electricity per mol ethylene produced, respectively). This is due to the higher inherent hydrogen production in the steam gasification process compared to oxygen gasification, resulting in steam gasification requiring only 2 moles while oxygen gasification requires 4 moles of external hydrogen to achieve the required carbon to hydrogen ratio. In the case of biomass technologies that use blue hydrogen, the total heat need for the steam gasification route was slightly higher (342 kJ/mol ethylene) than in the oxygen gasification-based route despite the latter requiring more external hydrogen. Note that for the blue hydrogen-based steam gasification route, heat is required for the two endothermic processes, i.e., 126 kJ heat is required for SMR hydrogen production and 216 kJ is required for steam gasification process. The biomass fermentation route assisted with direct electrochemical reduction of CO_2 to ethylene required the least electricity need (444 kJ/ mol ethylene) among the biomass process routes due to the higher efficiency of direct electrochemical reduction at ideal conditions.

The CUE of the biomass-based technologies shows that the SMR-based routes have higher values than the process with WGS hydrogen production routes. Theoretically, to produce 1 kg of hydrogen, 5.5 kg of CO_2 is produced by the SMR while 22 kg of CO_2 is produced by the water-gas-shift reaction (as part of the biomass gasification process). A comparison between biomass steam and oxygen gasification with blue hydrogen, shows that theoretically 0.79 kg of CO_2 and 1.57 kg of CO_2 are produced per kg ethylene respectively, due to the difference in external hydrogen needs. Thus, in the case of biomass, the use of blue hydrogen resulted in a decrease in the amount of direct CO_2 emissions compared to the technologies that do not use external hydrogen. This is because the SMR process has lower direct CO_2 emissions compared to the water gas shift process (as shown in the supplementary information in Table S11).

Table 9: Selected technologies from different hydrogen origins (internal and external) for plastic feedstock considering boundary-2 (Abbreviations: PHTP- Plastic high temperature pyrolysis, PLTP- Plastic low temperature pyrolysis, POSC- Pyrolysis oil steam cracking, PSG- Plastic steam gasification, FT- Fischer Tropsch, POG- Plastic oxygen gasification, WE- Water electrolysis (green hydrogen), SMR- Steam methane reforming (blue hydrogen), WGS- Water gas shift, DER- Direct electrochemical reduction, CM2E- CO to Ethylene). Note: The negative sign refers to energy production and the positive sign refers to energy need.

Routes	**Ideal stoichiometric reactions**	**CUE**	**kJ/mol ethylene**		
			EN	**HN**	**HP**
PHTP	$Polyethylene\ (-C_2H_4-)_n \xrightarrow[Depolymerisation]{} n\ C_2H_4$	100%	0	106	0
PSG + FT	$Polyethylene\ (-C_2H_4-)_n + 2n\ H_2O \rightarrow 2n\ CO + 4n\ H_2$ $2n\ CO + 4n\ H_2 \rightarrow n\ C_2H_4 + 2n\ H_2O$	100%	0	404	-298
PLTP + POSC	$Polyethylene\ (-C_2H_4-)_{6n} \xrightarrow[Pyrolysis]{} Naphtha\ (n\ C_{12}H_{24})$ $Naphtha(C_{12}H_{24}) \xrightarrow[Cracking]{} 2\ H_2 + CH_4 + C_2H_4 + C_3H_6 + C_6H_6$	100%	0	402	0
POG + FT +	$Polyethylene\ (-C_2H_4-)_n + n\ O_2 \rightarrow 2n\ CO + 2n\ H_2$ $n\ CO + 2n\ H_2 \rightarrow 0.5\ n\ C_2H_4 + n\ H_2O$	100%	409	0	-317

DER (CM2E)	$Cathode: CO + 2\,H_2O + 2\,e^- \rightarrow 0.5\,C_2H_4 + H_2O + 2\,OH^-$ $Anode: 2\,OH^- \rightarrow H_2O + 0.5\,O_2 + 2\,e^-$				
WE + POG + FT	$Cathode: 4n\,H_2O\; +\; 4n\,e^- \rightarrow 2n\,H_2 +\; 4n\,OH^-$ $Anode: 4n\,OH^- \rightarrow 2n\,H_2O + n\,O_2 + 4n\,e^-$ $Polyethylene\ (-C_2H_4-)_n + n\,O_2 \rightarrow\; 2n\,CO + 2n\,H_2$ $2n\,CO +\; 4n\,H_2 \rightarrow n\,C_2H_4 +\; 2n\,H_2O$	100%	474	0	-466
SMR + POG + FT	$Polyethylene\ (-C_2H_4-)_n + n\,O_2 \rightarrow\; 2n\,CO + 2n\,H_2$ $0.5n\,CH_4 + n\,H_2O \rightarrow 2n\,H_2 + 0.5n\,CO_2$ $2n\,CO +\; 4n\,H_2 \rightarrow n\,C_2H_4 +\; 2n\,H_2O$	80%	0	126	-466
POG + WGS + FT	$Polyethylene(-C_2H_4\,-)_{2n}$ $+3nO_2 \rightarrow 2n\,CO + 2n\,CO_2 + 4nH_2$ $2n\,CO +\; 4n\,H_2 \rightarrow n\,C_2H_4 +\; 2n\,H_2O$	50%	0	0	-1199

For waste plastic-based routes, there were five routes with internal hydrogen production (low temperature pyrolysis, high temperature pyrolysis, oxygen gasification with direct electrochemical steam gasification and oxygen gasification with WGS) and only one route with external hydrogen production (oxygen gasification without WGS). Considering the different hydrogen origins, seven technologies were selected in boundary-2 as shown in Table 9. Plastic low temperature pyrolysis (PLTP) technology requires the highest feed input (168 kg to produce 28 kg ethylene) while the other technologies require only 28 kg plastic feed to produce 28 kg ethylene at 100% CUE. This is because the PLTP technology produces naphtha (or pyrolysis oil) and to produce ethylene, the naphtha undergoes the cracking process which is a multi-product process producing other valuable hydrocarbons. The energy analysis shows that waste plastic-based technologies are endothermic except for oxygen gasification. Among the plastic-based routes, plastic high temperature pyrolysis and SMR with oxygen gasification routes required the least heat energy. For the oxygen gasification, using an external hydrogen source improved the CUE, as 3.14 kg of CO_2 is produced without external hydrogen while only 0.79 kg of CO_2 is produced with the blue hydrogen-based route, per kg ethylene produced (as shown in supplementary information Table S11). This is due to the low carbon intensity of the steam methane reformer (SMR) based hydrogen (5.5 kg of CO_2/kg H_2) compared to a water gas shift reaction-based hydrogen (22 kg of CO_2/kg H_2).

3.3 Multi-criteria assessment using boundary-1 and boundary-2

In the multi-criteria analysis; the boundary-1 and boundary-2 are compared using three pareto curves: electricity need, heat need and heat production vs carbon utilisation efficiency. The Pareto diagrams of electricity need vs carbon utilisation efficiency for boundary-1 (Figure 5 (a)) and boundary-2 (Figure 5 (b)) and heat need vs carbon utilisation efficiency for boundary-1 (Figure 6 (a)) and boundary-2 (Figure 6 (b)) shows the significance of the hydrogen origin assumption on technology screening . For boundary-1, only with hydrogen as an input stream, hydrogen import-based exothermic technologies like CO_2 hydrogenation to methanol and oxygen gasification of biomass or plastics appear more favourable over other technologies due to no energy needs and high carbon utilisation efficiencies for ideal reactions at standard temperature & pressure conditions. However, when considering boundary-2, the electricity need pareto front re-arranges into three distinct regions with waste plastic-based technologies in the centre of the pareto, as shown in Figure 5 (b). The pattern seen in the pareto front in boundary-2 is caused by the differences in hydrogen need of ACS feedstocks, i.e., the waste plastic-based technologies need the lowest amount of external hydrogen followed by biomass and CO_2. The hydrogenation of CO_2 to methanol and oxygen gasification of biomass or plastic, which performed better in terms of energy need and CUE in boundary-1, were not the best performing technologies in boundary-2. For instance, for CO_2 feedstock, the hydrogenation to methanol-based route requires the highest electricity or has the lowest CUE in boundary-2. Among the ACS-based technologies; SMR, oxygen gasification with WGS and anaerobic digestion-based route shows the least energy need while water electrolysis, direct electrochemical, steam gasification and pyrolysis-based routes show the highest CUE.

In the case of SMR-based processes, due to the differences in the hydrogen need of ACS feedstocks; biomass steam gasification and plastic oxygen gasification based technology which required 2 moles of external hydrogen (as shown in Table 8, Table 9 and supplementary information Table S11) performed better than CO_2 hydrogenation to methanol based process. Thus, among the SMR-based processes, the plastic oxygen gasification with SMR technology performed the best (as seen in Figure 6 (c)). Even though the CO_2 produced increased for technologies which required more SMR based external hydrogen, technologies like biomass oxygen gasification emitted the highest CO_2 which did not use any external hydrogen due to lower CUE of the process.

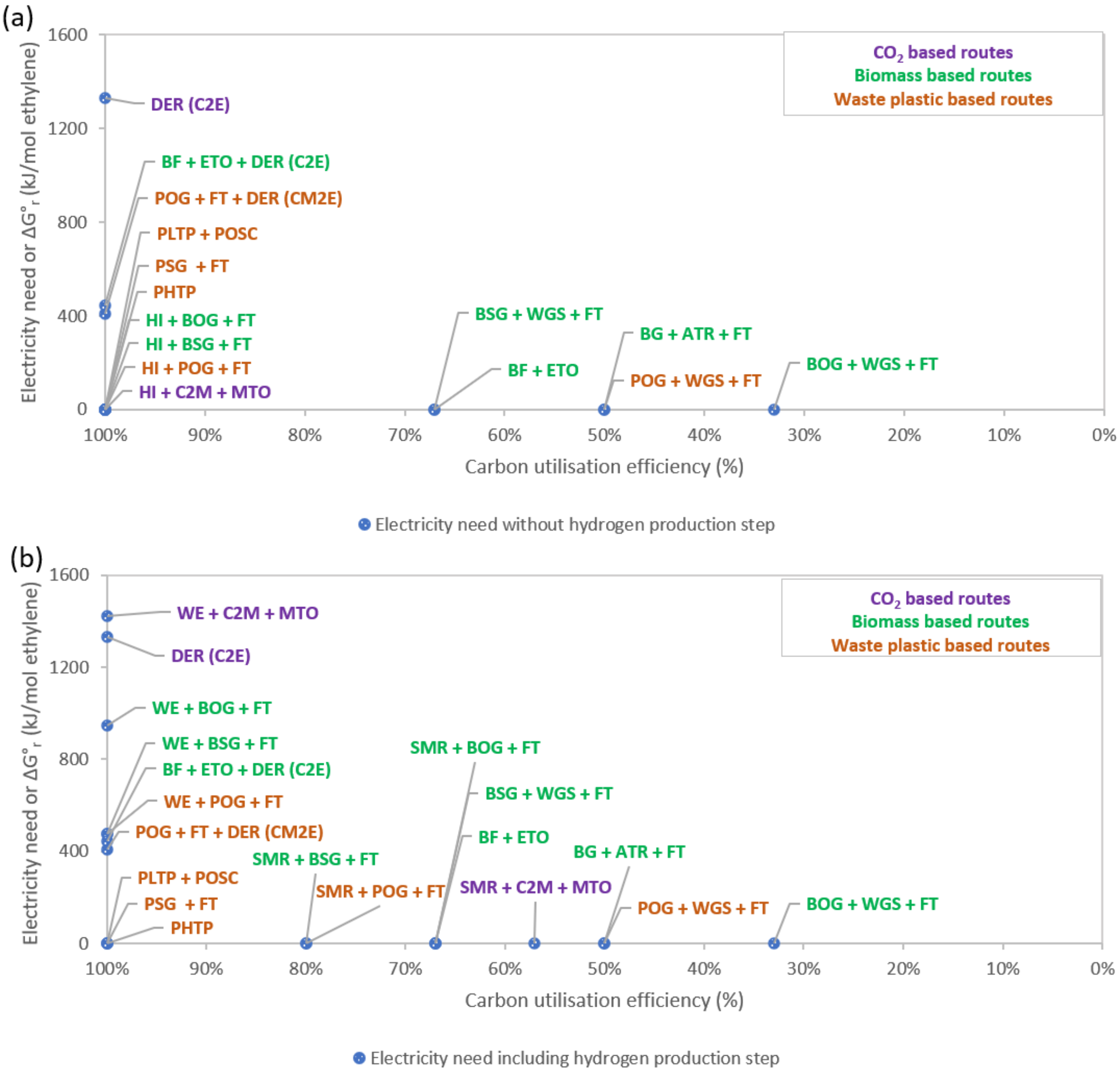

Figure 5: Pareto diagram of electricity need vs carbon utilisation efficiency for ACS-based ethylene production routes with different hydrogen origins for (a) boundary-1 and (b) boundary-2. (Abbreviations: DER- Direct electrochemical reduction, C2E- CO_2 to ethylene, CM2E- CO to ethylene, HI- Hydrogen import, WE-Water electrolysis, SMR- Steam methane reforming, C2M- CO_2 to methanol, MTO- Methanol to olefin, BSG- Biomass steam gasification, FT- Fischer Tropsch, BOG- Biomass oxygen gasification, BF- Biomass fermentation, BG- Biogas production, ATR- Autothermal reforming, ETO- Ethanol to olefin, PHTP- Plastic high temperature pyrolysis, PLTP- Plastic low temperature pyrolysis, POSC- Pyrolysis oil steam cracking, PSG- Plastic steam gasification, POG- Plastic oxygen gasification)

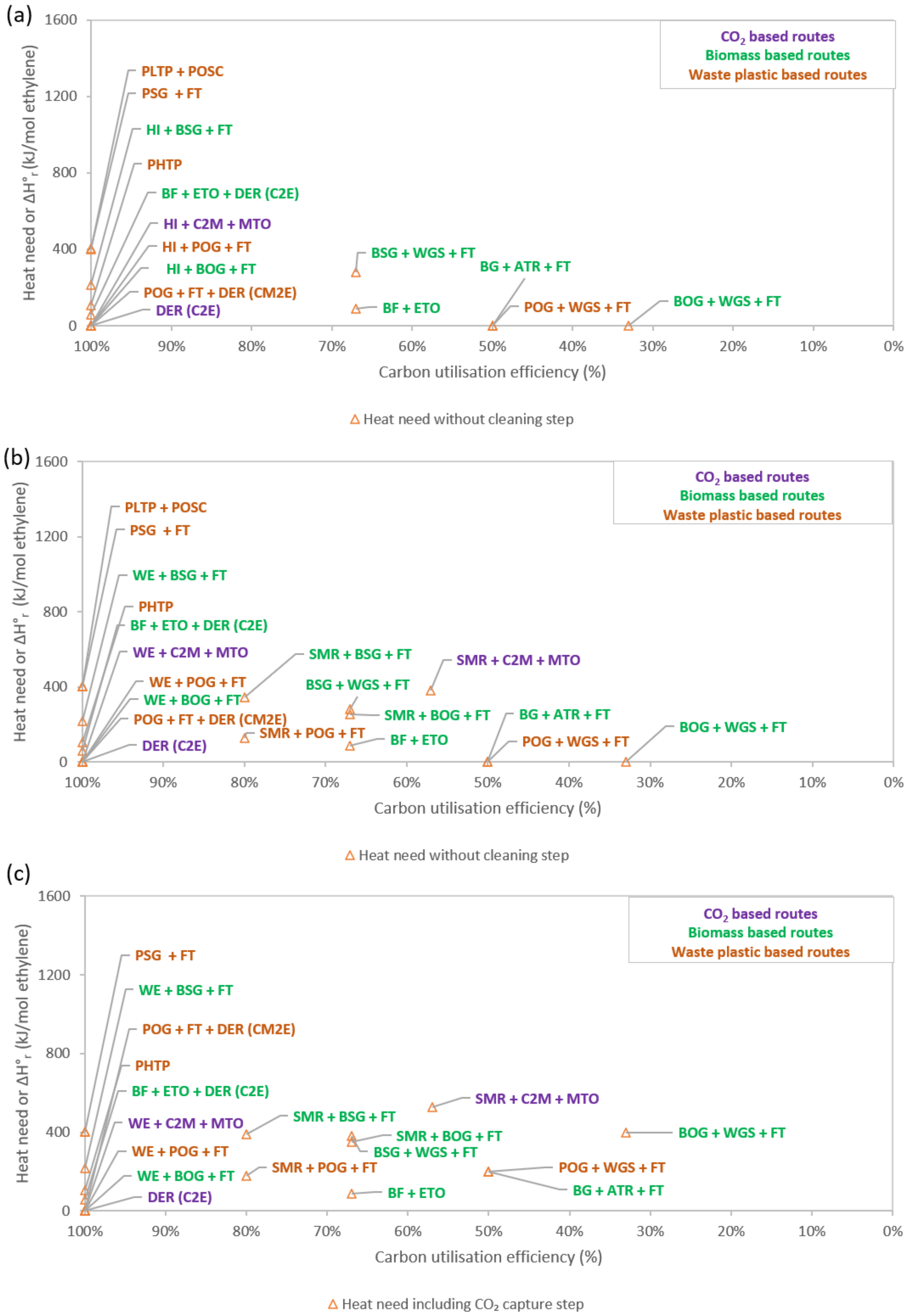

Figure 6: Pareto diagram of heat need vs carbon utilisation efficiency for ACS-based ethylene production routes with different hydrogen origins for (a) boundary-1, (b) boundary-2 without CO_2 separation step and (c) boundary-2 including CO_2 separation. (Abbreviations: DER- Direct electrochemical reduction, C2E- CO_2 to ethylene, CM2E- CO to ethylene, HI- Hydrogen import, WE-Water electrolysis, SMR- Steam methane reforming, C2M- CO_2 to methanol, MTO- Methanol to olefin, BSG- Biomass steam gasification, FT- Fischer Tropsch, BOG- Biomass oxygen gasification, BF- Biomass fermentation, BG- Biogas production, ATR- Autothermal reforming, ETO- Ethanol to olefin, PHTP- Plastic high temperature pyrolysis, PLTP- Plastic low temperature pyrolysis, POSC- Pyrolysis oil steam cracking, PSG- Plastic steam gasification, POG- Plastic oxygen gasification)

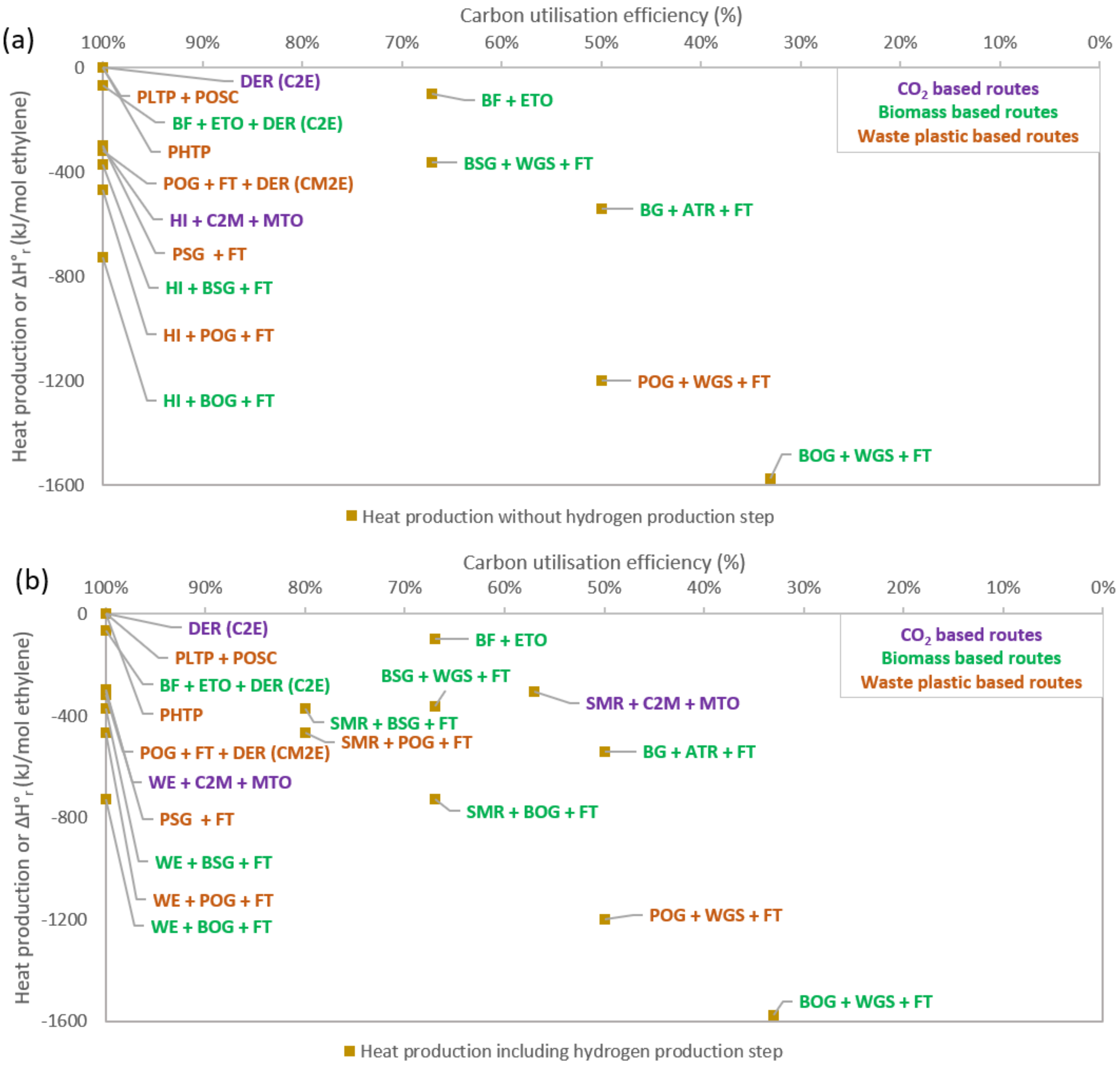

Figure 7: Pareto diagram of heat production vs carbon utilisation efficiency for ACS-based ethylene production routes with different hydrogen origins for (a) boundary-1 and (b) boundary-2. (Abbreviations: HI- Hydrogen import, DER- Direct electrochemical reduction, C2E- CO_2 to ethylene, CM2E- CO to ethylene, WE-Water electrolysis, C2M- CO_2 to methanol, MTO-Methanol to olefin, SMR- Steam methane reforming, BSG- Biomass steam gasification, FT- Fischer Tropsch, BOG- Biomass oxygen gasification, BF- Biomass fermentation, BG- Biogas production, ATR- Autothermal reforming, ETO- Ethanol to olefin, PHTP- Plastic high temperature pyrolysis, PLTP- Plastic low temperature pyrolysis, POSC- Pyrolysis oil steam cracking, PSG-Plastic steam gasification, FT- Fischer Tropsch, POG- Plastic oxygen gasification)

The comparison of heat need without cleaning step (Figure 6 (b)) and heat need including CO_2 capture step (Figure 6 (c)) for boundary-2 shows that the exclusion of CO_2 removal process step did not change the technology screening results compared to the impact of hydrogen on technology screening, due to the comparatively lower energy need of 100 kJ/mol CO_2 for carbon capture.

The pareto diagram of heat production vs carbon utilisation efficiency for boundary -1 (Figure 7 (a)) and boundary-2 (Figure 7(b)) shows that oxygen gasification-based technologies with hydrogen import or water electrolysis have better heat production with high CUE. Among the technologies, the oxygen gasification of biomass or waste plastic with WGS showed the highest heat production. The external hydrogen import had an impact on the CUE of these ACS-based technologies, compared to the results in boundary-1, but did not create a major change in the pareto front pattern, as seen for electricity need indicator. The comparison of the two boundaries illustrates how technology screening for ethylene synthesis changes with different hydrogen origin assumptions (as summarised in supplementary information section Table S10). The exothermic technologies based on hydrogenation and oxygen gasification performs better in boundary-1, while endothermic technologies like direct electrochemical reduction, steam gasification and pyrolysis perform better in boundary-2. Hence, the study implies that based on the boundaries considered the technology selection is affected drastically. This has broader implications for petrochemical industries or policy makers considering the defossilisation of the petrochemical feedstocks. For example, in the case of CO_2 feedstock by assuming hydrogen import, methanol to olefin technology seems promising in terms of material and energy indicators for ethylene production; while by including hydrogen production, direct electrochemical reduction of CO_2-H_2O to ethylene seems promising. Among the ACS feedstocks, with hydrogen import assumption; all the feedstocks seem equally superior while by considering hydrogen production, plastic outperforms other ACS feedstocks due to the inherent high hydrogen content in waste plastic.

4. Conclusions

This study explores the influence of hydrogen origin on the technology screening of alternative carbon-based ethylene production routes. From 70 possible pathways to make ethylene from CO_2, biomass and waste plastic, considering the different hydrogen generation technologies and boundaries (i.e., internal hydrogen production as part of the ACS-based process, external hydrogen supply with on-site production and hydrogen import), ethylene production technologies were selected using a short-cut screening methodology. The 70 possible pathways were screened to select one ethylene production route with a different hydrogen origin for each ACS feedstock. The selected pathways were analysed with material and energy indicators for ideal reaction at standard temperature & pressure conditions. The analysis showed that the hydrogen origin assumption had a significant impact on the material and energy indicators for ACS-based routes and thus influenced the technology screening. For example, assuming that hydrogen is imported (i.e., without considering the hydrogen origin or by considering hydrogen as input), short-cut methods would identify exothermic technologies based on hydrogenation of CO_2 to methanol and oxygen gasification of biomass or plastic waste as favourable over other routes because the material and energy penalties of the highly endergonic hydrogen production process are neglected. If, however, a company would consider producing the hydrogen onsite within the boundaries of the analysis, endergonic technologies like direct electrochemical reduction of CO_2-H_2O to ethylene, biomass steam gasification and waste plastic pyrolysis would appear more favourable, due to the higher material and energy efficiencies they have for hydrogen production compared to the other routes. Assumptions about hydrogen availability or origin tend to be made earlier on during the scoping phase and can significantly change the R&D portfolio. This is especially the case when assessing CO_2-based routes. The impact on biomass and waste plastics is present though less significant. Thus, the results of this study have broader implication for future petrochemical industries and policy makers; and highlights the significance of hydrogen for the selection of future ACS-based chemical production. The technologies selected in this chapter will be used for the process and cluster level techno-economic impact assessment in Chapter 4.

4. Rewiring petrochemical clusters: Impact of using alternative carbon sources for ethylene production

This chapter is based on the manuscript Manalal J. T., Pérez-Fortes M., & Ramírez A. (2025). Re-wiring petrochemical clusters: impact of using alternative carbon sources for ethylene production. Green Chemistry, 27(22), 6641–6659. https://doi.org/10.1039/D4GC06042C

Chapter specific nomenclature & symbols

Nomenclature

ACS	Alternative carbon source
BFW	Boiler feed water
BTX	Benzene, toluene and xylene
CAPEX	Capital expenditure
CBB	Chemical building blocks
CHP	Combined heat and power
CKI	Chloor Kringloop Installatie (or Chlorine incineration)
CUE	Carbon utilisation efficiency
CW	Cooling water
DEG	Diethylene glycol
EB	Ethylbenzene
EDC	Ethylene dichloride
EDTA	Ethylenediamine tetra-acetic acid
EG	Ethylene glycol
EO	Ethylene oxide
HHPS	High-high pressure steam
HPS	High pressure steam
HT	High temperature
IPA	Isopropyl alcohol
KPI	Key performance indicator
LLPS	Low-low pressure steam
LPS	Low pressure steam
MDI	Methylene diphenyl diisocyanate
MEG	Monoethylene glycol
MPS	Medium pressure steam
MSP	Minimum selling price
MTBE	Methyl tert-butyl ether
OPEX	Operational expenditure
PEM	Proton exchange membrane
PET	Polyethylene terephthalate
PFD	Process flow diagram
PGME	Propylene glycol methyl ether
PO	Propylene oxide
PoR	Port of Rotterdam
PTA	Purified terephthalic acid
PVC	Polyvinyl chloride
RME	Rapeseed methyl ester
ROI	Return on investment
SM	Styrene monomer
TBA	Tert-butyl alcohol
TEG	Triethylene glycol
TEEG	Tetra-ethylene glycol
TRL	Technology readiness level
VCM	Vinyl chloride monomer
VGO	Vacuum gas oil

Symbols

EUR/t	Euro per tonne
EUR/y	Euro per year
GW	Gigawatt
kt/y	Kilotonne per year
kW	Kilowatt
MJ/kg	Megajoule per kilogram
Mt	Million tonnes
MWh	Megawatt-hour
PJ/y	Petajoule
TJ/y	Tera joule per year
TWh	Terawatt-hour
V	Volt
wt%	Weight percentage

Abstract

To achieve climate change mitigation targets, defossilising the production of bulk chemicals like ethylene will be critical. These high-volume petrochemicals are typically produced from fossil-based feedstocks in industrial clusters, which are highly integrated in terms of mass and energy. Replacing fossil-based processes in interconnected industrial clusters can, therefore, impact such interactions and decrease performance or cause lock-in situations at the cluster level. This has, however, been overlooked in the literature. This chapter addresses this knowledge gap by evaluating the impacts of replacing fossil-based ethylene production in an existing industrial cluster with processes that use Alternative Carbon Sources (ACS) such as biomass, CO_2 and plastic waste . This study explicitly evaluates the performance of the ACS-based production routes at process and cluster levels by assessing changes in mass, energy, prices, CO_2 emissions and water demand. The results show that due to the notable difference in product distribution, energy needs and waste generation, a complete re-wiring of the petrochemical cluster in terms of mass, energy and revenue will be required. The results also indicate that defossilising ethylene production in existing industrial clusters can result in a shifting of burden outside the cluster for byproduct production, which can lead to increasing fossil-fuel use outside the cluster. At process level, the main challenges to defossilise ethylene are access to large quantities of clean energy and the large investment costs. Under current market conditions, among the different options examined, plastic pyrolysis is the most competitive ACS-based technology with the lowest impact at the cluster level. However, this requires a large availability of plastic waste , which will be challenging given current recycling rates. Further improvements in waste valorisation and integration of renewable energy-based heating will also be required to make this technology environmentally appealing.

1. Introduction

Defossilising[6] petrochemical feedstocks by using alternative carbon sources (ACS) such as CO_2, biomass, and waste plastic is key to achieving climate neutrality targets.[87,88] Today, about 85% of all chemicals produced globally are made from fossil sources.[89] Fossil-based feedstocks like methane and naphtha are currently used for producing chemical building blocks (CBB) like methanol, ethylene, propylene, benzene, toluene and xylene. These CBB chemicals can, however, also be produced from ACS-based feedstocks, which is expected to not only avoid fossil-fuel usage but also benefit the environment through carbon recycling. [2–4,42]

Several studies have looked into pathways, enablers and impacts of defossilising the chemical sector. For instance, Bazzanella et al.,[42] explored the transition of the European chemical industry to carbon neutrality. They identified several challenges, including the availability of low carbon energy and ACS feedstocks, high investment cost of ACS technologies, uncompetitive production costs of ACS-based chemicals and uncertainty regarding future policies.[2,42,90] They estimated the production costs of olefins from ACS-based processes to be two to five times higher than their fossil-based counterparts at current conditions[42]. They also concluded that for the European chemical industry to be carbon neutral by 2050, it will require around 4900 TWh low-carbon power, 50 to 300 Mt feedstock CO_2, 200 to 250 Mt dry lignocellulosic biomass, and an extensive additional investment of 800 to 900 billion Euro.[42] The range in the quantities of CO_2 and dry biomass is due to the differences in the intermediate (up to 59% reduction in CO_2 emissions) and ambitious (more than 95% reduction in CO_2 emissions) scenarios for the chemical industries in Europe.[42] Vogt et al.,[91] analysed possible pathways to make sustainable fuels (like diesel, kerosene) and chemicals (like olefins, aromatics) by defossilising all refineries by 2050 at global-level. They concluded that about 1400 Mt biomass (with a molecular weight of 30 g/mol C) and 630 Mt plastic waste (with a molecular weight of 14 g/mol C) will be needed to defossilise the 615 refineries worldwide. Kahler et al.[4] also pointed out that recycling (including chemical and mechanical recycling) will be the most important carbon source by 2050 and could contribute up to 55% of the global required carbon in the chemical industry. Their study acknowledged that the main type of ACS can change throughout regions due to feedstock availability, energy availability, access to technology, market conditions and that there will not be a one-size-fits-all solution.

Although these type of global level studies provide broad perspectives regarding the global impact of defossilising the chemical industry, location specific studies have also been conducted to understand the techno-economic and environmental impact of ACS at a regional level. As an example, Stork et al.,[8] analysed potential pathways to reduce 80-95% of greenhouse gas emissions in the Dutch chemical industry. They showed that using ACS feedstocks will be vital to reduce non-energy related (scope-1 and scope-3) emissions by 2050 and that around 26 Billion Euro will be required.[8] Schijndel et al.[59] examined a portfolio of technologies that included electrolysis, pyrolysis, gasification, fermentation, Fischer-Tropsch and methanol synthesis for the Dutch chemical production. They showed that by 2050, around 35 Mt of biomass and recycled plastic will be needed. The study also highlighted that even if the current renewable energy ambitions of the Netherlands would be achieved (70 GW wind and 100 GW solar energy by 2050), this would not be enough, as the required renewable energy demand by a defossilised chemical industry was estimated at 300 TWh. In a more site-specific study, Samadi et al[52] explored defossilisation options for chemical industries in the Port of Rotterdam (PoR). They considered water electrolysis, gasification, syngas hydrogenation and pyrolysis to produce base chemicals. The study showed that by 2050, about 9 Mt of dry biomass and 20-50 TWh of low carbon electricity are required to achieve carbon neutrality.[52] Even though these studies provide valuable insights regarding the pathways and bottlenecks for the transition of the Dutch chemical sector; they do not provide insights regarding the impacts of transitioning CBB chemicals in existing industrial clusters.

Among the CBB chemicals, ethylene has the largest global production[64] and the highest CO$_2$ emissions during production, due to the energy-intensive process of naphtha or ethane steam cracking.[92] Manuel et al.,[92] analysed the defossilisation of the Dutch CBBs, including ethylene, and found that synthetic naphtha from waste plastic was the preferred choice for high-value chemical production due to the significantly lower levelised cost of production compared to bio-based or hydrogen-based routes. However, currently, only 9% to 14% of plastics are globally recycled, and studies suggest that by 2050, a circular economy approach could only meet 20% to 30% of the synthetic naphtha demand.[55,90,93] Hence, other technologies such as methanol to olefins are gaining interest to fulfil future defossilisation goals for ethylene production.[93–95] Those studies have also shown that, without integrating ACS feedstock change along with renewable energy, the ACS technologies could result in a net increase in emissions and have unintended environmental impacts.[3]

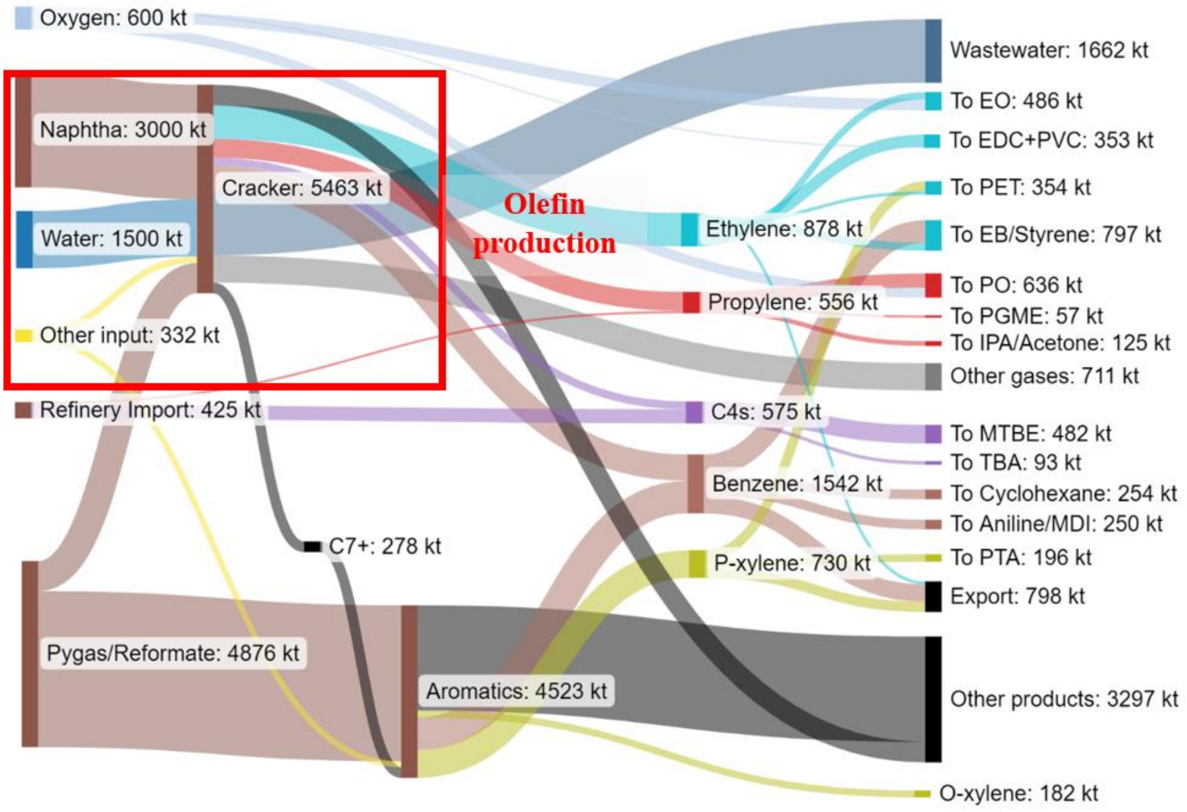

Figure 1. Example of material flows in a conventional fossil-based petrochemical cluster for the production of ethylene (Abbreviations: EO- Ethylene oxide, EDC- Ethylene dichloride, PVC- Polyvinyl chloride, PET- Polyethylene terephthalate, EB- Ethylbenzene, PO- Propylene oxide, PGME- propylene glycol methyl ether, IPA- Isopropyl alcohol, MTBE-Methyl tert-butyl ether, TBA- Tert-butyl alcohol, MDI- Methylene diphenyl diisocyanate, PTA- Purified terephthalic acid).

There are, however, several important considerations present in state-of-the-art studies[7,55,59], including those discussed before, which require further attention. First, simplified models of the production processes, including black box and linear models are often used, partly due to the low technology readiness level (TRL) of most ACS-based processes. A low TRL level implies high uncertainties in data, leading to large variations in the techno-economic and environmental impacts. For example, pyrolysis oil from waste plastic has different hydrocarbon fractions[96] and the current naphtha steam crackers can handle only a part of this hydrocarbon fraction (i.e., hydrocarbon in the boiling range of 35 to 180 °C).[97] Studies such as by Schijndel et al.,[59] assumed that the whole pyrolysis oil can be used as feedstock for ethylene production, which will lead to lower estimates of waste plastic needs or CO$_2$ emissions. Other studies such as Thunman et al[98] focuses on defossilising the olefin plant in an existing setting using plastic recycling (high temperature pyrolysis), although, the results look promising, key aspects in the product profile like ethylene to propylene ratio and its impact on downstream units are generally overlooked.[98]

Second, chemical production plants are not stand-alone systems, as they produce by-products which are generally used as a feedstock or a source of energy by other units or plants (as shown in Figure 1). Replacing the fossil feedstock will not only have techno-economic and environmental impacts for the process that is replaced, but might also cause cluster-level impacts due to the high system integration in the chemical sector[91]. Chemical production plants are generally allocated in industrial clusters, where mass and energy flows are exchanged with other plants.[99] Third, for the proper functioning of a chemical production plant, auxiliary units such as combined heat and power (CHP) plants, steam systems, and cooling water systems are critical.[100] Any change in production processes due to the use of ACS feedstock can impact equipment land footprint, scope-2 CO_2 emissions and secondary water demand. To date, these impacts have not been well studied in the literature[34,48–50,52,101–108].

This chapter aims to address these three knowledge gaps, by evaluating the techno-economic impacts of displacing fossil-based ethylene production in an existing industrial cluster with processes that use ACS feedstocks. This study explicitly evaluates the performance of the production routes at process and cluster levels by assessing changes in (1) the dependency on import and/or export (changes in mass and energy flows in the cluster), (2) cascading impact of changes in ethylene price throughout different value-chains, (3) changes in CO_2 emissions and water demand.

2. Methodology

To study the impacts of defossilising ethylene production in an existing petrochemical cluster, the current situation in the Port of Rotterdam (PoR) was used as a point of departure (reference case cluster). Potential ACS-based processes to produce ethylene were identified and modelled, mimicking industrial scale capacities. Impacts were evaluated both at process and cluster levels. Further details are provided below.

2.1 Reference case: Fossil-based ethylene cluster

Material, energy and economic data for the reference case were obtained from an in-house model of a petrochemical cluster in the PoR as described in Tan et al.,[99]. Each individual process was modelled at plant level in Aspen Plus v12. In total, the in-house model includes 57 chemical processes and their energy islands. In this study, we focus on the ethylene cluster, as shown in Figure 2 (The red, blue and green lines represent ethylbenzene, ethylene oxide and ethyl dichloride value-chains).

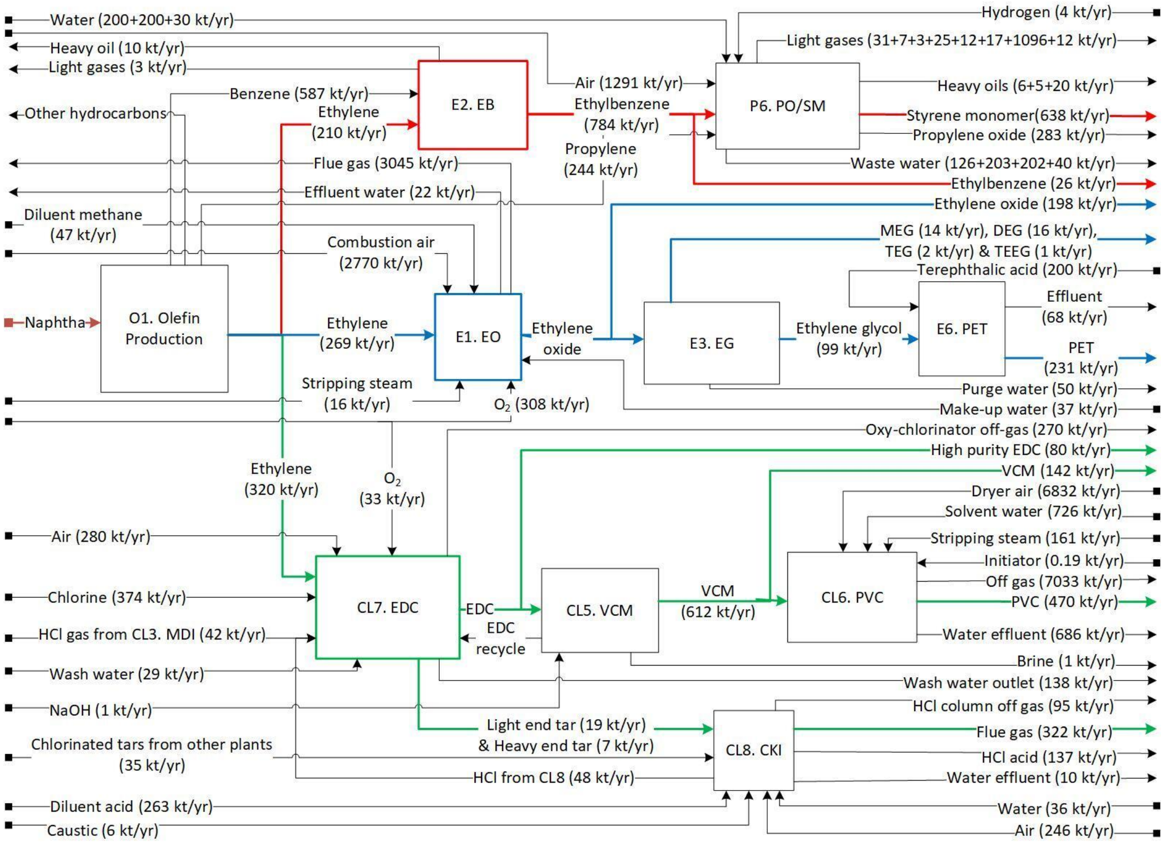

Figure 2. Mass flows in the reference case ethylene cluster (Abbreviations: EO- Ethylene oxide, EDC- Ethylene dichloride, PVC- Polyvinyl chloride, PET- Polyethylene terephthalate, EB- Ethylbenzene, PO- Propylene oxide, SM- Styrene monomer, EG- Ethylene glycol, MEG: Monoethylene glycol, DEG: Diethylene glycol, TEG: Triethylene glycol, TEEG: Tetra-ethylene glycol, VCM- Vinyl chloride monomer, CKI- Chlorine incineration). The numbers in brackets indicates the mass flow in kt/y.

The naphtha steam cracker in the reference case produces about 900 kt/y ethylene, 500 kt/y propylene and 700 kt/y benzene. Steam cracking involves the high-temperature pyrolysis (at 850 °C) of saturated hydrocarbons in the presence of steam.[109] During steam cracking, a wide range of lower hydrocarbons are produced, mainly methane, ethylene, ethane, acetylene, propylene, propane, butene, butadiene, benzene, toluene, xylene, ethylbenzene, methyl hexane and methyl heptane.[109] After the steam cracking (as shown in Figure 3), the hydrocarbon mixture undergoes downstream purification to remove impurities (e.g. CO_2, H_2S, H_2O) followed by complex separation processes (e.g., high pressure cryogenic distillation and extractive distillation) to separate the individual components into high purity products.[109] Figure 3 shows the simplified block flow diagram of the model used in this study. The detailed process flow diagram (PFD), modelling assumptions, mass balance, energy balance, economic calculations and data sources is provided in Zenodo repository (links provided in SI).

In the in-house petrochemical cluster, we explicitly model the energy islands mimicking existing conditions in the PoR. Note that in many cases the existing energy islands provide steam and electricity to more than one process. Figure 4 shows the energy island of the reference olefin plant, which includes the electricity, heating and cooling flows / needs, the associated flows of energy to different processes,

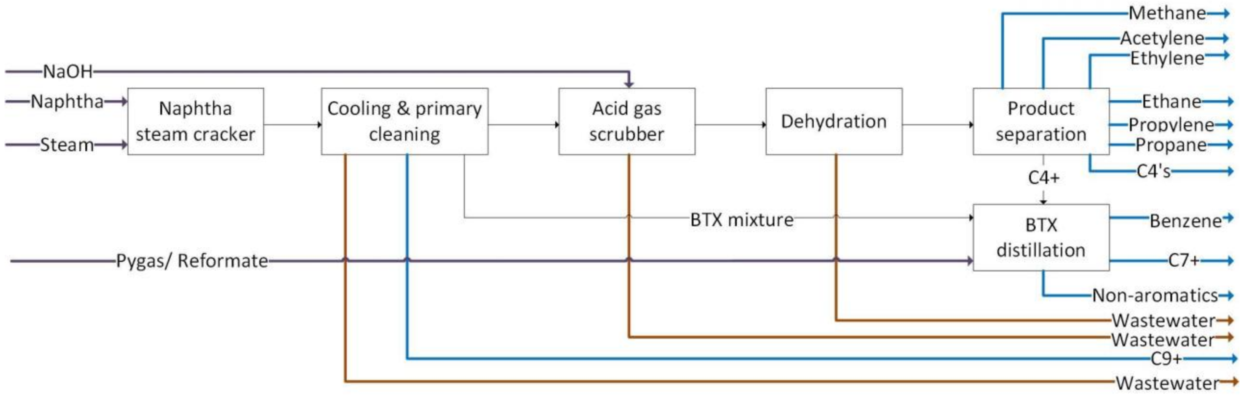

Figure 3. Block flow diagram of Naphtha steam cracker process (Abbreviation: BTX- Benzene, toluene and xylene)

and the CHP plant. Further detailed of energy and mass balances of the different processes can be seen in Tan et al[99].

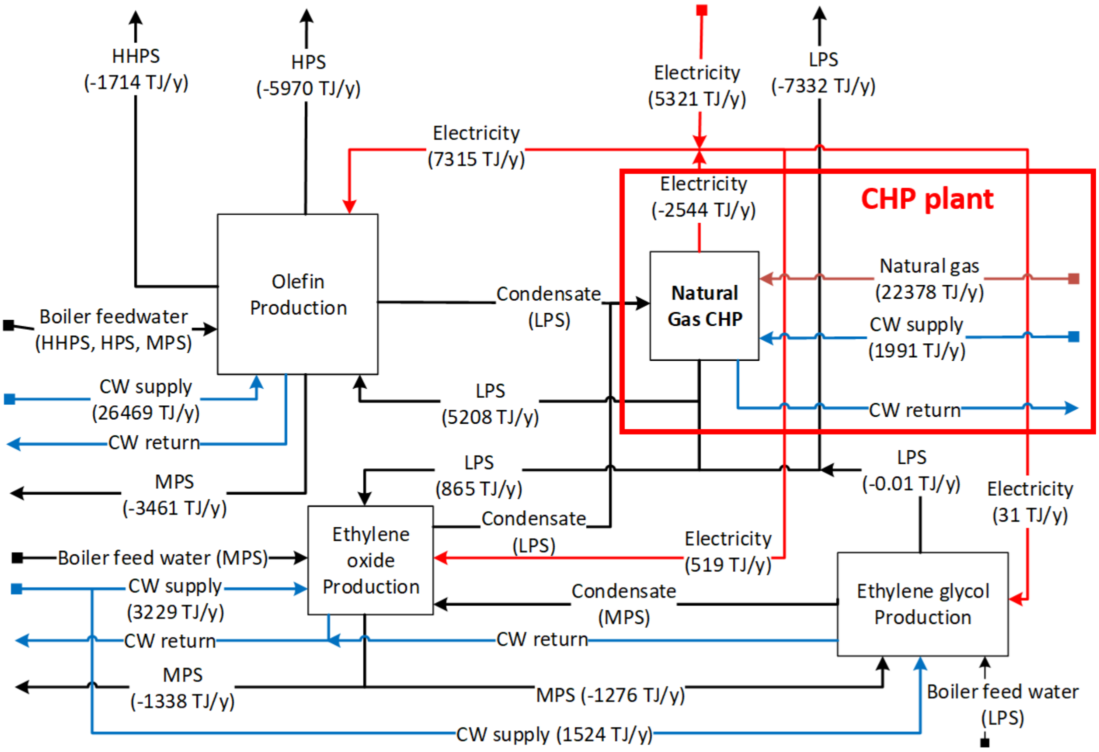

Figure 4. Energy island of reference case fossil-based petrochemical cluster for the production of ethylene (Note: Negative sign refers to heat or electricity production and positive sign refers to heat or energy need)

2.2 Ex-ante ACS process modelling

To defossilise ethylene production, ACS-based ethylene production processes were modelled to match the 900 kt/y ethylene demand in the cluster. Table 1 shows the six ACS-based ethylene production routes that were included in this study together with the TRL of the different steps. For the ACS-based processes, due to time and resource constrains, only two promising technologies from each feedstock were selected using the screening methodology which considered the indicators TRL, number of reaction steps, ideal heat and electricity needs; based on the screening methodology in Chapter 2.[79]

The technologies in the ACS-based processes were modelled using Aspen Plus and Aspen Economic Analyzer V12. All models reached an ethylene purity of 99.9 wt% and have a production capacity of about 300 kt/y, equivalent to 1/3rd of the demand in the PoR, which is ambitious for ACS-based technologies while still being industrially relevant capacities.[99] The performance of the different routes were evaluated at process and cluster level for 300 kt and 900 kt ethylene/y, respectively, using the indicators explained in section 2.3. A short description of the different technologies in each route is provided in SI section S2 and the detailed assumptions, mass balance, energy balance, economics and data sources for each technology can be found in the Zenodo repository (links provided in SI).

Table 1. ACS-based processes for ethylene production included in this study

Alternative Carbon Source technologies and their TRLs		
CO_2 routes	**Biomass routes**	**Waste plastic routes**
Direct electrochemical - Direct electrochemical reduction of CO_2-H_2O to ethylene [TRL=4]	**Fischer Tropsch + methanol to olefin** - Biomass steam gasification to syngas [TRL=7] - Water electrolysis [TRL=8] - Syngas to Fischer Tropsch * [TRL=9] - CO_2 hydrogenation to methanol * [TRL=7] - Methanol to olefin * [TRL=8]	**Pyrolysis + cracking** - Plastic low temperature pyrolysis [TRL=7] - Water electrolysis [TRL=8] - Pyrolysis oil steam cracking [TRL=7]
Methanol to olefin - CO_2 hydrogenation to methanol [TRL=7] - Water electrolysis [TRL=8] - Methanol to olefin [TRL=8]	**Methanol to olefin** - Biomass steam gasification to syngas [TRL=7] - Water electrolysis [TRL=8] - Syngas to methanol [TRL=9] - Methanol to olefin [TRL=8]	**Methanol to olefin** - Plastic steam gasification to syngas [TRL=8] - Syngas to methanol [TRL=9] - Methanol to olefin [TRL=8]

Note: * The Fischer Tropsch and methanol to olefin based production processes occur in parallel and the process configuration is detailed in SI section S2.

2.3 Process and cluster level impacts

ACS processes for ethylene production were compared using techno-economic and environmental key performance indicators (KPIs). At process level*,* KPIs were based on process complexity, process performance, utility needs, economics, CO_2 emissions and water demand (as shown in Table 2*)*. The ACS-based processes to produce ethylene were first analysed as stand-alone using process level KPIs. In a second step, they were introduced into the reference case cluster by substituting the fossil-based plant and compared using the material and energy flows between the reference and ACS case. This approach allowed us to understand the disruption on material and energy connections in the cluster. To simplify the assessment, it is assumed that excess energy, products, waste and raw materials needed or produced due to the defossilisation are available, usable or treatable outside the cluster, and are included in the OPEX calculations when relevant. At cluster level, the KPIs used were based on changes in mass flow, energy flow, price, CO_2 emissions and water demand with respect to the reference case (as shown in Table 2).

Table 2. Process and cluster level techno-economic and environmental KPIs considered in this study.

Assessment level	**Key performance Indicators**		
	Technical	**Economic**	**Environmental**

Process level	• Process complexity (process temperature range, process pressure range, single pass conversion, bare equipment area) • Product yields and product purity • Heating, cooling and electricity (utility needs)	• CAPEX • OPEX • Minimum selling price (MSP)	• Scope-1 and scope-2 CO_2 emissions • Primary and secondary water demand • Carbon utilisation efficiency (CUE)
Cluster level	Import or export dependency impacts (feed, products, utility): • change in mass flows* • change in energy flows*	• CAPEX • Change in MSP *	• Scope-1 and scope-2 CO_2 emission • Primary and secondary water demand

Note: *Change with respect to the reference case

All processes were modelled in Aspen Plus considering the heating and cooling utilities as given in Table 3. The heat integration strategy used in this study was to heat or cool the process streams step-wise using the different utilities, to calculate the net utility need or production.

Table 3. Heating and cooling utilities considered in this study

Heating utilities		**Cooling utilities**	
Type	**Conditions**	**Type**	**Conditions**
R50 generation	Saturated vapor to liquid methane at 1.02 bar	HHPS generation	Saturated liquid to steam at 500 °C and 100 bar
R1150 generation	Saturated vapor to liquid ethylene at 1.02 bar	HPS generation	Saturated liquid to steam at 51 bar
R134a generation	Saturated vapor to liquid 1,1,1,2-Tetrafluoroethane at 1.02 bar	MPS generation	Saturated liquid to steam at 21 bar
Chilled water generation	16 wt% propylene glycol-water mixture from 7.5 °C to 5 °C at 1.02 bar	LPS generation	Saturated liquid to steam at 5.5 bar
Low-low pressure steam (LLPS)	Saturated steam to liquid at 3.9 bar	LLPS generation	Saturated liquid to steam at 3.9 bar
Low pressure steam (LPS)	Saturated steam to liquid at 5.5 bar	Cooling water	25 °C to 40 °C at 1.02 bar
Medium pressure steam (MPS)	Saturated steam to liquid at 21 bar	Chilled water	16 wt% propylene glycol-water mixture from 5 °C to 7.5 °C at 1.02 bar
High pressure steam (HPS)	Saturated steam to liquid at 51 bar	R134a	Saturated liquid to vapor 1,1,1,2-Tetrafluoroethane at 1.02 bar
High-high pressure steam (HHPS)	Steam at 500 °C and 100 bar to saturated liquid	R1150	Saturated liquid to vapor ethylene at 1.02 bar
Natural gas or high temperature (HT) utility	81.4 wt% methane, 1 wt% CO_2, 14.4 wt% N_2, 3 wt% ethane, 0.2 wt% propane at 15 °C and 1.02 bar	R50	Saturated liquid to vapor methane at 1.02 bar

Note: HT utility– High temperature utility is used when the heat need is greater than 350 °C and in this study natural gas with a lower heating value of 37.8 MJ/kg was used.

CAPEX was calculated departing from the bare equipment costs obtained from Aspen Economic Analyzer for the different unit models and using estimates from Towler & Sinnott[100] (as shown in Appendix B Table B7). The fixed OPEX estimate was based on Towler & Sinnott[100] (as shown in Appendix B Table B7). The variable OPEX was calculated based on mass and energy flows obtained from the Aspen Plus models. Price data[110,111] was adjusted to the base year 2018 by using the chemical producer price index[112] (as given in SI Table S7). The equipment life was assumed 25 years except in the case of proton exchange membrane (PEM) water electrolysers (9 years)[113] and CO_2 electrolysers (assumed to be 5 years based on past industrial scale PEM electrolyser equipment life)[114]. Only the electrolyser stack was replaced during the plant life and both the electrolyser stack cost was assumed to be 30% of total electrolyser cost.[115] The minimum selling price (MSP) was calculated for 8% return on investment (ROI) with CAPEX, OPEX and revenue. For multi-product processes, the MSP was calculated by using revenue allocation[79] as explained in Chapter 2.[79] The price calculation using the revenue allocation was used only for the hydrocarbon product streams.

To calculate the scope-2 emissions of both the fossil-based and ACS-based processes, a natural gas based combined heat and power (CHP) plant with a CO_2 intensity of 0.076 ktonne CO_2/TJ for electricity and 0.073 ktonne CO_2/TJ for steam were used. Furthermore, a renewable electricity source was assumed in addition to the CHP plant, to assess its impact on the CO_2 emission results. The assessment of this study does not include scope-3 emissions.

The primary water demand was calculated for each process by summing up the process water needs, for instance, as gasifying agent, stripping steam, dilution water and electrolysis water. To calculate the secondary water demand (defined in this study as the sum of make-up water for utilities); the cooling water and boiler feed water make-up needs were calculated. The cooling water make-up need was calculated by assuming a 2% make-up due to evaporation and blowdown losses[116]. The boiler feed water (BFW) make-up need was calculated by assuming 25% make-up due to blowdown and condensate losses.[117] Other water demand associated with feedstocks (like water need for biomass cultivation) were not considered in this study.

The carbon utilisation efficiency definition was introduced in Chapter 2.[79] It is defined as the ratio between the amount of carbon in the products and the amount of carbon in the feedstock (equation 1).

$$Carbon\ utilisation\ efficiency\ (CUE) = \frac{\sum_{m=1}^{m=q} Mass\ flow\ of\ \text{elementary}\ carbon\ in\ product\ (m)}{\sum_{n=1}^{n=r} Mass\ flow\ of\ \text{elementary}\ carbon\ in\ feedstock\ (n)} \tag{1}$$

Where, m: stands for the products, q for the numbers of products, r is the number of feedstocks and n stands for the carbon feedstock.

Note that the change in MSP in the cluster looks at the cascading impact on the prices of downstream products in the value chain as a consequence of changes in the price of ethylene. This type of assessment was introduced in Chapter 2 (equation 2) and assumes that for the downstream value-chains, the price increase in ethylene or its derivatives is compensated by a price increase in their respective products, to maintain the same gross margin.[79]

$$\sum_{i=1}^{i=a} \Delta Product\ Price\ (i) * Product\ mass\ flow(i) = \sum_{j=1}^{j=b} \Delta Raw\ material\ Cost\ (j) * Raw\ material\ mass\ flow(j) \tag{2}$$

Where, i stands for the products, a for the number of products, j is the raw material, and b the number of raw-materials.

2.4 Scenario analysis

As most ACS-based routes are not yet commercial (as given in Table 1), data is highly uncertain. To explore the impact of uncertainty due to the data inputs and modelling assumptions on the calculated ethylene price of ACS-based processes, a scenario analysis was done. Only the uncertainty of ethylene price is discussed in this chapter, as the main focus of this study was on ethylene production and because the prices of other by-products vary in the same percentage due to the use of the revenue allocation approach. For the scenario analysis, the main contributing factors from OPEX and CAPEX analysis were identified. Based on these major contributing factors and the main underlying assumption behind these factors, the scenario analysis on ethylene MSP was conducted by varying these assumptions within the state-of the-art upper and lower limit values (Table 4).

Table 4. Variables used for the scenario analysis with their upper and lower limits (Abbreviations: RME: Rapeseed methyl ester, PEM: Proton exchange membrane, EDTA: Ethylenediamine tetra-acetic acid)

Variables used	Upper limit	Lower limit
Return on investment	12%	4%
Food grade CO_2 price	300 EUR/t	80 EUR/t
Biomass pellet price	400 EUR/t	50 EUR/t
Sorted waste plastic price	800 EUR/t	400 EUR/t
Unsorted waste plastic price	500 EUR/t	100 EUR/t
RME solvent price	1000 EUR/t	350 EUR/t
Direct CO_2-H_2O to ethylene reduction electrochemical cell operating voltage	3.65 V	2 V
Direct CO_2-H_2O to ethylene reduction electrochemical cell operational life	25 years	5 years (with 50% component replacement)
Direct CO_2-H_2O to ethylene reduction electrochemical cell cost	1500 EUR/kW	580 EUR/kW
PEM water electrolyser operating life	25 years	9 years (with 50% component replacement)
PEM water electrolyser cost	1060 EUR/kW	580 EUR/kW
Electricity price	84 EUR/MWh	11 EUR/MWh
EDTA solvent price	1340 EUR/t	500 EUR/t

3 Results and discussion

3.1 Impacts of using ACS in the ethylene process

The ACS-based routes show considerable differences in techno-economic and environmental performances compared to the reference case (as shown in Table 5 and Table 6) and indicates that the defossilisation of ethylene production, is more than just equipment change.

In terms of mass flow, the ACS-based processes show significantly different raw-material needs, product distribution and waste generation due to the difference in feedstock elemental composition (as shown in Tables B1, B2, B3 and B4 in Appendix B) and process efficiencies (Table 5). The differences also exist when looking at the same ACS feedstock. For instance, to produce the same quantity of ethylene, plastic waste pyrolysis requires almost 2.7 times higher feedstock than the plastic based methanol to olefin route. This is because even though the carbon utilisation efficiency of pyrolysis route

(74%) is higher than that of the plastic methanol to olefin process (67%), the ethylene yield in the former case (6%) is considerably lower than the methanol to olefin-based process (18%). This can be explained by the differences in by-product production as shown in Table 6.

In terms of product distribution, the plastic based pyrolysis process is most similar to the reference case and the CO_2 based direct electrochemical process has the least similarity, as the CO_2 based direct electrochemical process is a single product technology while the others are multi-product based technologies. This difference in product distribution can impact downstream units in a highly interconnected cluster, which is discussed in section 3.2.

Table 5. Process level annual mass flow comparison of different ACS-based ethylene production processes.

Parameter		**Carbon Source**						
		Naphtha	**CO_2 based**		**Biomass based**		**Plastic based**	
		Reference case	**Direct electrochemical**	**Methanol to olefin**	**Fischer Tropsch + methanol to olefin**	**Methanol to olefin**	**Pyrolysis + cracking**	**Methanol to olefin**
Raw materials	Carbon feedstock	1034 kt (Naphtha)	1510 kt (CO_2)	4800 kt (CO_2)	6900 kt (Biomass)	5160 kt (Biomass)	5000 kt (Sorted plastic waste)	1860 kt (Municipal plastic waste)
	Water or Steam	568 kt	2241 kt	5886 kt	6907 kt	5286 kt	813 kt	1320 kt
	Other feedstocks	279 kt	-	-	35 kt	18 kt	278 kt	-
Products	Ethylene	303 kt	329 kt	314 kt	301 kt	314 kt	303 kt	314 kt
	Propylene	172 kt	-	398 kt	298 kt	398 kt	172 kt	398 kt
	Benzene	237 kt	-	80 kt	136 kt	80 kt	237 kt	80 kt
	Other hydrocarbon products	363 kt	7 kt	335 kt	716 kt	647 kt	3173 kt	347 kt
	Oxygen	-	1955 kt	5226 kt	2533 kt	2004 kt	128 kt	-
Waste	Wastewater	573 kt	1338 kt	2735 kt	7056 kt	5315 kt	573 kt	1325 kt
	Hydrocarbon waste	-	-	1488 kt	112 kt	-	-	-
	Purge or off-gas	233 kt	122 kt	100 kt	1360 kt	712 kt	1035 kt	256 kt
	Char or ash	-	-	10 kt	1158 kt	868 kt	470 kt	88 kt
	Tar	-	-	-	172 kt	126 kt	-	372 kt
Process carbon utilisation efficiency		84%	69%	68%	39%	48%	74%	67%
Ethylene yield (Ethylene to carbon feedstock mass %)		29%	22%	7%	4%	3%	6%	18%

Table 6. Detail of product mass flows of the different ACS-based processes (Abbreviations: VGO: Vacuum gas oil)

Product mass flow	**Carbon Source**						
	Naphtha	**CO_2 based**		**Biomass based**		**Plastic based**	
	Reference case	**Direct electrochemical**	**Methanol to olefin**	**Fischer Tropsch + methanol to olefin**	**Methanol to olefin**	**Pyrolysis + cracking**	**Methanol to olefin**
Methane	143 kt	-	10 kt	248 kt	274 kt	143 kt	10 kt
Acetylene	6 kt	-	-	-	-	6 kt	-
Ethane	43 kt	-	9 kt	-	9 kt	43 kt	9 kt
Ethylene	303 kt	329 kt	314 kt	301 kt	314 kt	303 kt	314 kt
Ethanol	-	7 kt	-	-	-	-	-
Propane	4 kt	-	74 kt	55 kt	74 kt	4 kt	74 kt
Propylene	172 kt	-	398 kt	298 kt	398 kt	172 kt	398 kt
C4 mixture	74 kt	-	106 kt	154 kt	106 kt	74 kt	106 kt
Benzene	237 kt	-	80 kt	136 kt	80 kt	237 kt	80 kt
Diesel	-	-	-	-	-	1456 kt	-
VGO	-	-	-	-	-	1333 kt	-
C7+	101 kt	-	-	161 kt	-	101 kt	-
C9+	77 kt	-	-	-	-	77 kt	-
Non-aromatics	101 kt	-	-	98 kt	-	101 kt	-
Oxygen	-	1955 kt	5226 kt	2533 kt	2004 kt	-	-

In terms of energy requirements (Table 7), most ACS-based processes produce sufficient heat energy from off-gas combustion and are energy self-sufficient in terms of heat, except for the plastic based methanol to olefin process. This process requires around 15 PJ/y additional high-temperature heat energy (>900 °C) and 17 PJ/y low-pressure steam, which are almost 8 to 10 times higher than the reference case. The high heat requirements are mostly due to two reasons: the high specific energy need for gasification and the low calorific value of off-gases. For example, the plastic based methanol to olefin process has a reaction energy of 11 MJ/kg ethylene, and the off-gas of the process has a lower net calorific value of 27 MJ/kg; compared to the reaction energy of 13 MJ/kg ethylene and lower net calorific value of 52 MJ/kg off-gas for the naphtha cracker. This low calorific value for the off-gas from plastic based methanol to olefin process is due to the presence of partially oxidised molecules like CO and CO_2 from gasification in the off-gas. To compensate for the low heating value, additional external heat or gas is thus needed in the plastic based methanol to olefin process. In the biomass-based process, even though the heat need is high (~100 MJ/kg ethylene or 30-40 PJ/y), there are significant amounts of off-gases and waste hydrocarbons, which can be internally combusted for energy. Consequently, the biomass-based processes are net heat producers.

The CO_2 based methanol to olefin route has the highest electricity need among all processes, which is almost 62 times higher than the reference case. Of this amount, about 92% of the requirement is for hydrogen generation through water electrolysis (as shown in Figure 5). In the case of the biomass-based steam gasification route, it requires less electricity for hydrogen production through water electrolysis compared to the CO_2 based routes as shown in Figure 5. However, due to presence of impurities (like methane) in the syngas, the biomass-based processes required more electricity for cryogenic distillation. As a consequence, the CO_2 and biomass-based routes show similar electricity needs of around 80-150 PJ per year.

An aspect that is often overlooked is the physical area that new processes would require. This is particularly important when considering their implementation in existing industrial clusters. In the SI (Table S9), the bare equipment areas of the different routes are shown. To produce about 300 kt/y ethylene, the biomass-based route has the largest land footprint while CO_2 based direct electrochemical process has the lowest. Note that compared to the reference case, all the ACS-based processes require more bare equipment area. In densely populated clusters, such as the PoR, this indicate that physical constrains can affect the potential of technologies.

It is also worth mentioning that even though all the process routes produced 99.9 wt% pure ethylene, their impurities are different (as shown in Table S10 SI). For example, in the reference case ethylene have impurities like acetylene, methane and ethane at ppm levels, while the CO_2 based direct electrochemical route have CO_2 and ethanol. These changes in impurities could potentially affect downstream units, and further research into these impacts needs to be conducted.

Table 7. Utility needs and production of different ACS-based processes for 300 kt/y ethylene production (Note: Negative sign refers to heat production and positive sign refers to cooling, heating or electricity need respectively)

Utility need or production	**Carbon source**						
	Naphtha	**CO_2 based**		**Biomass based**		**Plastic based**	
	Reference case	**Direct electrochemical**	**Methanol to olefin**	**Fischer Tropsch + methanol to olefin**	**Methanol to olefin**	**Pyrolysis + cracking**	**Methanol to olefin**
Electricity	2.5 PJ/y	83.5 PJ/y	156.6 PJ/y	117.1 PJ/y	79.3 PJ/y	6.1 PJ/y	6.4 PJ/y
LLPS	-	-	-0.5 PJ/y	0.7 PJ/y	-0.5 PJ/y	-	-
LPS	1.8 PJ/y	-.6 PJ/y	-4.9 PJ/y	-23.4 PJ/y	-4.9 PJ/y	-3.1 PJ/y	17.3 PJ/y
MPS	-1.2 PJ/y	-1.2 PJ/y	-2.7 PJ/y	-2.4 PJ/y	-7.9 PJ/y	-4.2 PJ/y	-9.4 PJ/y
HPS and HHPS	-2.7 PJ/y	-	-0.01 PJ/y	-30.3 PJ/y	-19.3 PJ/y	-33.6 PJ/y	-3.8 PJ/y
HT utility	-	-	-	-	-	-	15 PJ/y
Cooling water	9.1 PJ/y	15.7 PJ/y	46.1 PJ/y	10 PJ/y	73.5 PJ/y	12.8 PJ/y	25.5 PJ/y

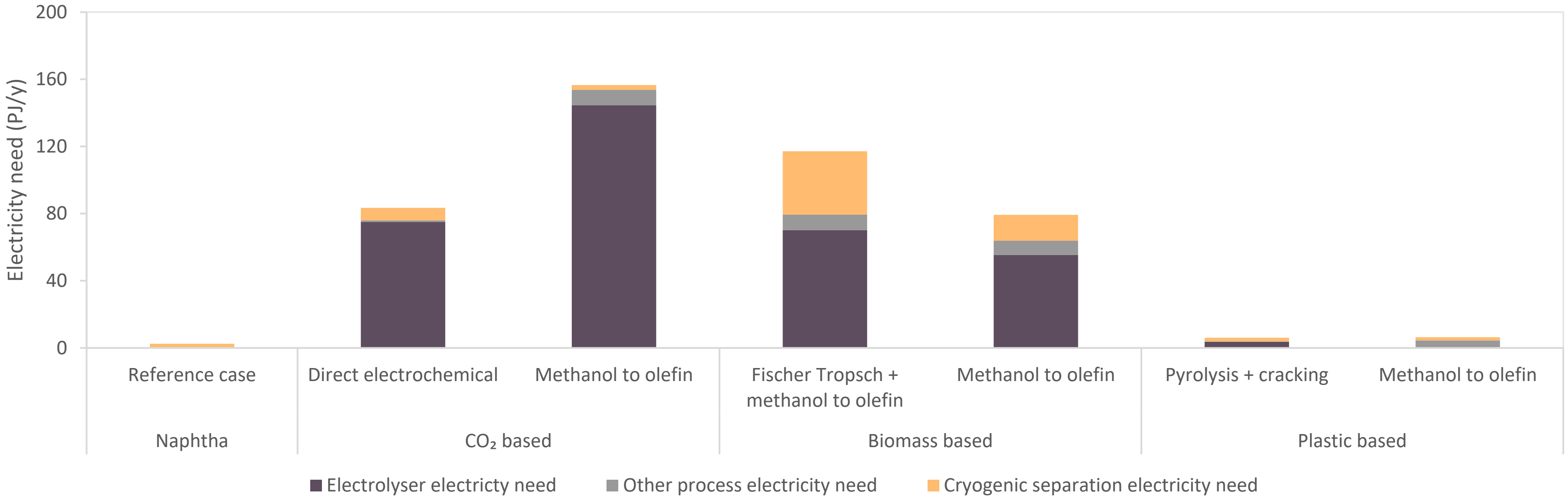

Figure 5. Electricity needs of different ACS-based processes for 300 kt/y ethylene production

The results from the economic analysis show that with exception of plastic pyrolysis, all other ACS-based processes are not competitive under current market conditions (as seen in Table 8). The CO_2 based route shows the highest MSP, followed by biomass and plastic. In fact, plastic pyrolysis shows a similar price to the reference case (1075 EUR/t) due to higher CUE and lower CAPEX. A key reason for the higher MSP of ethylene in most ACS processes is that they tend to be more CAPEX and OPEX intensive than the reference route. In absolute terms, the CAPEX investment can be as high as 45 times (CO_2 based methanol to olefin route) higher than a conventional naphtha cracker. In all the CAPEX intensive ACS-based routes, hydrogen production accounts for a major share of the costs (as seen in SI Figure S25 to Figure S38). For example, in the CO_2 based direct electrochemical process, the electrolyser alone accounts for 54% and in the methanol to olefin-based process the water electrolyser accounts for ~30% of the total CAPEX.

The OPEX intensity of the ACS-based routes is due to feedstock price and or utility costs (as seen in SI Figure S25 to Figure S38). In the reference case, raw material cost accounts for about 84% of the OPEX, while utilities account for only 12% of the OPEX. For the CO_2-based process, the cost of raw material becomes comparatively minor (5% of the OPEX), while utilities account for 53% to 63% of the total OPEX. For the biomass-based process, both raw material and utilities show a similar contribution (31%-40% and 36%-47%, respectively). Finally, for the plastic waste-based routes, raw material cost accounts for 90% and 64% of the OPEX for pyrolysis and plastic based methanol to olefin processes, respectively. The results indicate that the processes which are utility dominant (like CO_2 and biomass-based routes) tend to have the highest OPEX intensity compared to those that are feedstock dominant processes (like plastic and fossil-based processes). It is important to note that this can change if feedstock availability is constrained.

It is also important to highlight that for the ACS-based processes, the revenues from by-products are higher than the reference case except for the CO_2 based direct electrochemical route (as given in SI Table S11). In the reference case, for instance, while ethylene revenue has the highest contribution 33% to the total revenue; for the plastic based pyrolysis route, ethylene contributed only 9% of the total revenue. For the CO_2 based direct electrochemical process, the exception is due to the limited by-products. For methanol to olefin-based processes due to the higher propylene to ethylene production ratio compared to the reference case, the propylene contribution to revenue increased and became significantly higher than ethylene (~30% in methanol to olefin-based vs 17% in reference case).

Table 8. Economic comparison of different ACS-based processes for 300 kt/y ethylene production

Economic indicators	Carbon source						
	Naphtha	CO_2 based		Biomass based		Plastic based	
	Reference case	Direct electrochemical	Methanol to olefin	Fischer Tropsch + methanol to olefin	Methanol to olefin	Pyrolysis + cracking	Methanol to olefin
Ethylene MSP (EUR/t)	1,075	15,588	7,504	4,752	5,268	1,075	2,511
CAPEX (Million EUR)	390	15,803	17,743	12,766	12,619	1,532	2,737
OPEX (Million EUR/y)	850	3,719	5,872	5,998	5,330	3,616	2,400

In terms of process level CO_2 emissions (scope-1), the CO_2 based direct electrochemical emits the least CO_2 of all routes (95 kt/y) as seen in Figure 6. Notably, all the other processes emit more direct CO_2 than the reference case (633 kt CO_2/y). This higher emission is due to off-gas, char and fuel combustion for high temperature heat or waste to energy recovery in these processes. Thus, for the ACS-based processes, valorisation of off-gas and char to valuable products rather than waste to energy recovery, along with availability of high-temperature renewable heat will be critical for improving their environmental impact. It is important to note that there is a difference in the origin of emissions, while in the reference case, those are of fossil origin, in the ACS routes the emissions have different origins. In the case of biogenic emissions, whether they are considered "neutral" will depend on the type and value chain of the biomass. Emissions from waste plastic are so far considered "free" of environmental footprint as they are a waste (following gate-to-gate life cycle analysis guidelines), whether the same principle can be applied to waste to chemical concepts is still under debate. In the case of CO_2, the origin will play a key role in how the emissions are considered as they could originated from fossil processes, biogenic processes or the atmosphere (direct air capture).

In terms of water consumption, in all cases, the ACS-based processes need more process water than the reference case. The biomass-based processes require a larger amount than CO_2-based processes (Figure 7). This is because in this study, a steam dilution ratio (kg steam/kg biomass) of 0.59 is used in the simulation based on GoBiGas gasification technology[118], where 46% to 54% of the process water is needed as gasifying medium. Based on this assumption, biomass steam gasification uses about 13 to 11 times higher process water than a naphtha cracker, while the CO_2 based process needs around 10 to 4 times higher process water. The plastic-based methanol to olefin process has around 3.7 times higher water requirement, while the plastic-based pyrolysis process needs the least quantity of process water (1.5 times).

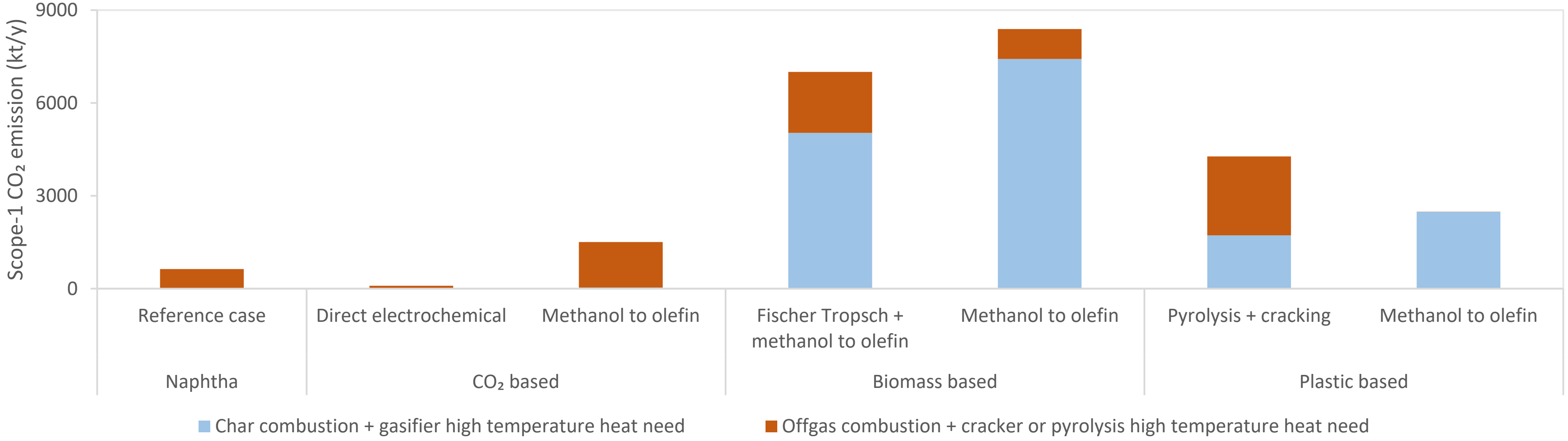

Figure 6. Scope-1 CO_2 emissions of different ACS-based processes for 300 kt/y ethylene production

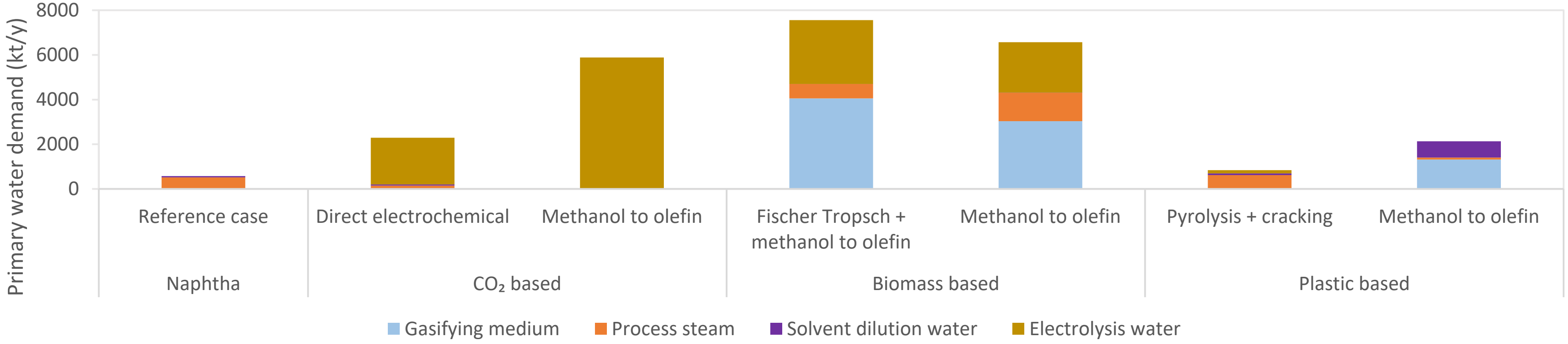

Figure 7. Primary water demand of different ACS based processes for 300 kt/y ethylene production

3.2 Cluster level impacts of defossilising the ethylene production

The results indicated that a notable number of flows within the cluster will be significantly affected due to the introductions of ACS processes (e.g., up to 22 mass flows change by more than 100%). This affects both upstream and downstream units interconnected to the olefin plant. The magnitude of this change varies based on the ACS process used, as seen in Table 9 and 10, Figure S39 to S44 in the SI. Hence, defossilising ethylene production in an existing petrochemical cluster is not just limited to changes in process technology but will have larger consequences in terms of mass flow and infrastructure investments.

Similar to the results at process level, Table 9 shows considerable variations of ACS feedstock needs to produce similar quantities of ethylene, as the carbon utilisation efficiency and ethylene yield of these technologies are different. For example, to produce 1 kg ethylene almost 15 kg CO_2 are needed in the methanol to olefin-based route compared to c.a. 5 kg CO_2 in the direct electrochemical based process. This significant variation in CO_2 need is due to the material inefficiencies in the CO_2 hydrogenation to methanol and methanol to olefin process (i.e., high recycle purge needs in methanol reactor (10%) and lower ethylene yield in methanol to olefin process (31%)). However, this does not mean all methanol to olefin-based routes will need higher feedstock. In contrast to the results of the CO_2 based routes, to produce 1 kg ethylene; the plastic based methanol to olefin process needs around 6 kg plastic compared to 16 kg plastic in the pyrolysis-based process. This is mainly because, in the plastic based pyrolysis route, the plastic to ethylene yield is 6% compared to 18% in the methanol to olefin-based process, which is due to the high yield of by-products in the pyrolysis process. Therefore, based on the ACS process used, the upstream material infrastructure in the cluster has to be specifically designed. Another possibility is to increase the olefin yield from pyrolysis-based process in the secondary cracking[97] from by-products like diesel and VGO or by using high temperature (direct)[98] pyrolysis-based processes. However, the current limitation of the high temperature pyrolysis-based process is its low TRL and need to replace the cracker reactor in the olefin plant.[98]

In addition to these changes, replacing the naphtha cracker for ACS-based ethylene production can also have an unintended effect on imports of other (fossil-based) chemicals in the cluster (as seen in Table 9 and Table S13 SI). For instance, the direct electrochemical route does not produce propylene, benzene and C7+ by-products, all of which are important chemical building blocks (CBB) in the cluster. Hence, if these building blocks are not sourced from a sustainable feedstock, it can lead to an increase in fossil feedstock use outside the cluster, to compensate for their lack of production in the cluster, leading to shifting of burden from inside the cluster to outside the cluster. In terms of climate change, it would mean that while the cluster itself could reduce its dependence on fossil feedstocks, the total emissions (estimated as the sum of emissions in and outside the cluster) could increase, thereby taking us farther away of reaching climate targets.

Table 9. Comparison of inlet mass flow changes at cluster level of different ACS-based ethylene production process

Mass flow per unit ethylene (kg/kg)		Carbon source						
		Naphtha	CO_2 based		Biomass based		Plastic based	
		Reference case	Direct electrochemical	Methanol to olefin	Fischer Tropsch + methanol to olefin	Methanol to olefin	Pyrolysis + cracking	Methanol to olefin
In	Naphtha	3.4	0.0	0.0	0.0	0.0	0.0	0.0
	Pygas/ Reformate	5.6	4.1	4.3	4.5	4.3	5.4	4.3
	Water	1.7	6.8	18.7	22.9	16.8	2.7	4.2
	CO_2	0.0	4.6	15.3	0.0	0.0	0.0	0.0
	Biomass	0.0	0.0	0.0	22.9	16.4	0.0	0.0
	Plastic	0.0	0.0	0.0	0.0	0.0	16.5	5.9
	Other input	0.4	0.2	0.2	0.3	0.2	0.2	0.2
	Refinery (Propylene)	0.1	0.6	0.0	0.0	0.0	0.0	0.0
	Refinery (C4s)	0.4	0.6	0.3	0.1	0.3	0.4	0.3
	Refinery (Benzene)	0.0	0.7	0.5	0.3	0.5	0.0	0.5
	Refinery import (C7+)	0.0	0.3	0.3	0.0	0.3	0.0	0.3
	Oxygen	0.7	0.0	0.0	0.0	0.0	0.2	0.6

Table 10. Comparison of outlet mass flow changes at cluster level of different ACS-based ethylene routes

Mass flow per unit ethylene (kg/kg)		**Carbon source**						
		Naphtha	**CO_2 based**		**Biomass based**		**Plastic based**	
		Reference case	**Direct electrochemical**	**Methanol to olefin**	**Fischer Tropsch + methanol to olefin**	**Methanol to olefin**	**Pyrolysis + cracking**	**Methanol to olefin**
Out	Ethylene	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Propylene	0.6	0.0	1.3	1.0	1.3	0.6	1.3
	Refinery (Propylene)	0.1	0.6	0.0	0.0	0.0	0.0	0.0
	C4s	0.2	0.0	0.3	0.5	0.3	0.2	0.3
	Refinery (C4s)	0.4	0.6	0.3	0.1	0.3	0.4	0.3
	Benzene	0.8	0.0	0.3	0.5	0.3	0.8	0.3
	Refinery (Benzene)	0.0	0.7	0.5	0.3	0.5	0.0	0.5
	Benzene (from aromatics plant)	1.0	0.9	0.9	0.9	0.9	0.9	0.9
	P-xylene	0.8	0.7	0.8	0.8	0.8	0.8	0.8
	O-xylene	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	Other products	0.6	0.0	0.0	1.3	0.0	9.9	0.0
	Other products (from aromatics plant)	3.1	2.8	2.9	3.1	2.9	3.0	2.9
	C7+ excess	0.0	0.0	0.0	0.2	0.0	0.0	0.0
	Wastewater	1.9	4.1	8.7	23.4	16.9	1.9	6.5
	Other waste	0.0	0.0	5.1	9.3	5.4	5.0	0.0
	Ethanol	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Oxygen	0.7	5.9	16.6	8.4	6.4	0.7	0.6
	Other gases	0.8	0.4	0.7	0.0	1.7	0.0	0.8

Table 10 shows the changes in mass flow downstream of the olefin plant in the cluster due to ethylene defossilisation. The most affected downstream mass flows in the cluster are wastewater, off-gases, heavy hydrocarbon and oxygen. Except for plastic based pyrolysis, in all other processes, the wastewater production increases from as low as 100% to as high as 1000%. Hence, new wastewater treatment facilities will be required in the cluster. Regarding other utilities, with exception of the waste plastic routes, in all other processes, oxygen production increases between 1000% to 2500%. Therefore, further studies need to explore potential avenues to exploit the high quantity of oxygen. In most processes, except for the CO_2 based direct electrochemical and waste plastic-based methanol to olefin, the amount of off-gas and/or heavy hydrocarbons increases in the cluster. This will require additional infrastructure to utilise these hydrocarbon streams for waste to heat recovery, waste to power or as new sources of sustainable feedstock for fuels or chemicals.

The ACS routes significantly affected the energy flows in the cluster. The reference case naphtha cracker has 6 inlet and outlet energy streams, and all these energy streams are affected when the unit is replaced with an ACS-based technology (as seen in Table 11, Figure S45 to Figure S50 SI). These impacts vary from non-use of existing energy infrastructure, to changes in the amount of energy, which can be as large as 650 times in energy flows into the cluster. The most impacted energy streams are cooling water flow, electricity flow and high pressure steam generation flow. The high cooling water flow, for example in the biomass route, is due to the high temperature reactions and distillation-based separation used in these processes. Noted that cooling water requirements could be further decreased by more exhaustive heat integration.

Table 11. Utility needs at cluster level of different ACS-based ethylene production processes (Note: Negative sign refers to heat production and positive sign refers to cooling, heating or electricity need respectively)

Utility flow per unit ethylene (MJ/kg)		**Carbon source**						
		Naphtha	**CO_2 based**		**Biomass based**		**Plastic based**	
		Reference case	**Direct electrochemical**	**Methanol to olefin**	**Fischer Tropsch + methanol to olefin**	**Methanol to olefin**	**Pyrolysis + cracking**	**Methanol to olefin**
In	LLPS	0	0	0	2	0	0	0
	LPS	6	0	0	0	0	0	55
	MPS	0	0	0	0	0	0	0
	HPS	0	0	0	0	0	0	0
	HHPS	0	0	0	0	0	0	0
	CW	30	48	147	332	234	42	81
	HT utility	0	0	0	0	0	0	16
	Electricity	8	254	498	389	253	20	20
Out	LLPS	0	0	-1	2	-2	0	0
	LPS	0	-2	-16	-78	-15	-10	55
	MPS	-4	-4	-9	-8	-25	-14	-30
	HPS	-7	0	0	-101	-61	-109	-12
	HHPS	-2	0	0	0	0	-2	0

The change in ethylene production from fossil naphtha to ACS-based processes will also have economic impacts (as seen in Table S14 SI) as changes in price of products or byproducts propagate in a cluster through value-chains. Among the ACS routes, the CO_2 based ethylene is the most expensive followed by biomass-based ethylene and waste plastic-based ethylene showing the lowest price increase.

Table 12 shows the propagation of the change in cost of ethylene in the value chains. For instance, ethylene is used to produce EDC, which in turn is the main raw material for VCM and VCM is then used to produce PVC (as shown in SI Table S15). In this route, CO_2 based direct electrochemical process results in an increase in MSP of ethylene of about 1350% which then cascades throughout the chain resulting in an increase on PVC MSP of about 982% (assuming all other products and utilities do not change in price). The impact is highly depending on the importance of ethylene as carbon source in the chain. The CO_2 based direct electrochemical process, for instance, affects only the ethylene-based value chains due to the lack of carbon by-products while the CO_2 based methanol to olefin route affects the ethylene, propylene and partially benzene value-chains. The partial impact in benzene value-chain is due to the insufficient production of benzene in the ACS-based processes with respect to the demand in the cluster. Among the ethylene value-chains, PVC is impacted the most based on the CO_2 process used. This large impact is due to ethylene being the only carbon source for PVC while in other value-chains this is not the case. Among the biomass-based process, the Fischer Tropsch + methanol to olefin route has a slightly higher impact on the PO-SM value-chain than the methanol to olefin-based process as the yield of benzene is slightly higher for Fischer Tropsch + methanol to olefin-based process than the methanol-based process. Compared to CO_2, the price impact of biomass-based process is lower. The plastic-based pyrolysis process shows no price impact on the value-chains, as it could produce naphtha at the market price of fossil-based naphtha (~560 EUR/t). The plastic-based methanol to olefin process creates an increase between 30% to 130% in the value-chains (as shown in Table 12 and SI Table S15).

Regarding CO_2 emissions, the indirect (scope-2) emission analysis of the ACS-based processes shows that, as these processes are highly energy intense, scope-2 emissions will be substantially high if existing (fossil) based energy mix is used (as seen in Figure 9). The major share of scope-2 CO_2 emissions is due to the electricity carbon footprint used and if renewable electricity is used, scope-2 emissions are considerably lowered. Replacing fossil-based feedstocks with ACS-based feedstocks requires therefore not only changing technology at plant level, but also major changes in utility infrastructure for the ACS-based processes to be environmentally appealing. It is important to note that this is not the case for waste plastic-based processes as these routes do not need external hydrogen production due to the better C/H ratio found in plastic feedstock.

The analysis of the impact on water demand of the cluster due to the ACS-based processes shows that secondary water demand by the cluster also increases, similar to what is observed for primary water demand at process level discussed in the previous section. The highest demand is observed for biomass-based processes in terms of cooling water due to their low-temperature cooling demand (cooling demand between 40 °C and 140 °C). Substantial cooling water and boiler feedwater demand is observed for all ACS-based processes compared to the reference case (as seen in Figure 10). Hence major infrastructural change in terms of cooling water and boiler feed water will be required to accommodate the new ACS-based processes.

Table 12. Minimum selling price (MSP) impact in the value chain of ACS-based processes (Note: In brackets the percentage change in price with respect to the reference case is shown)

Price impact in the value-chain (EUR/t)	**Carbon source**						
	Naphtha	**CO_2 based**		**Biomass based**		**Plastic based**	
	Reference case	**Direct electrochemical**	**Methanol to olefin**	**Fischer Tropsch + methanol to olefin**	**Methanol to olefin**	**Pyrolysis + cracking**	**Methanol to olefin**
Polyvinyl chloride (PVC)	740	8009 (+982%)	3959 (+435%)	2581 (+249%)	2840 (+284%)	740 (No price change)	1459 (+97%)
Polyethylene terephthalate (PET)	1284	5691 (+343%)	3236 (+152%)	2401 (+87%)	2557 (+99%)	1284 (No price change)	1720 (+34%)
Styrene monomer (SM)	1328	4439 (+234%)	5293 (+299%)	4006 (+202%)	3913 (+195%)	1328 (No price change)	2214 (+67%)
Propylene oxide (PO)	1450	4847 (+234%)	5780 (+299%)	4375 (+202%)	4275 (+195%)	1450 (No price change)	2417 (+67%)
Propylene glycol methyl ether (PGME)	800	No propylene production	1666 (+108%)	1295 (+62%)	1364 (+70%)	800 (No price change)	994 (+24%)
Acetone	856	No propylene production	5888 (+588%)	3734 (+336%)	4137 (+383%)	856 (No price change)	1980 (+131%)

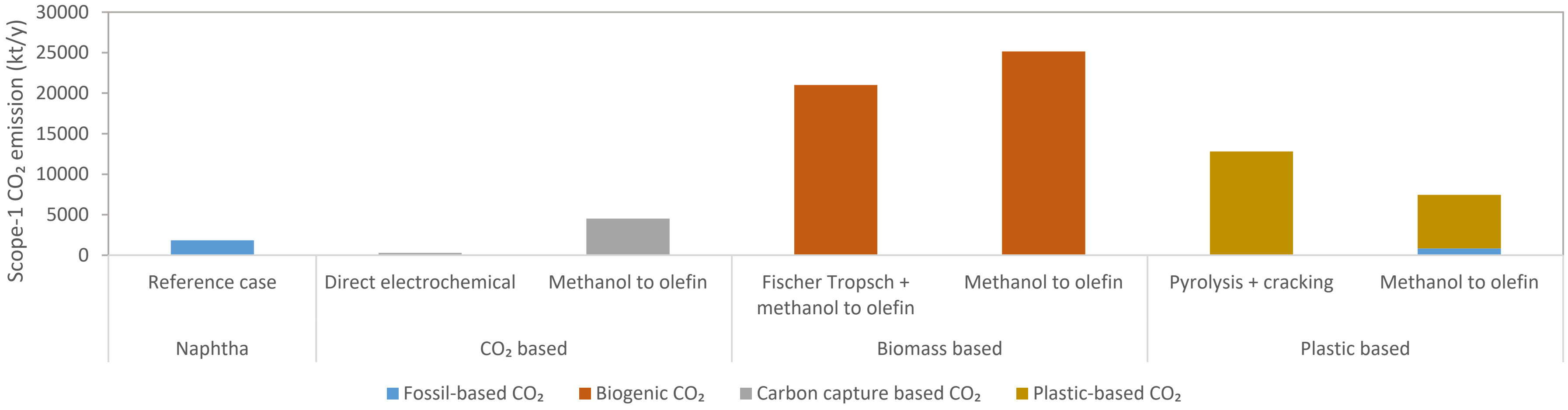

Figure 8. Scope-1 CO_2 emission of different ACS-based technologies for 900 kt/y ethylene production

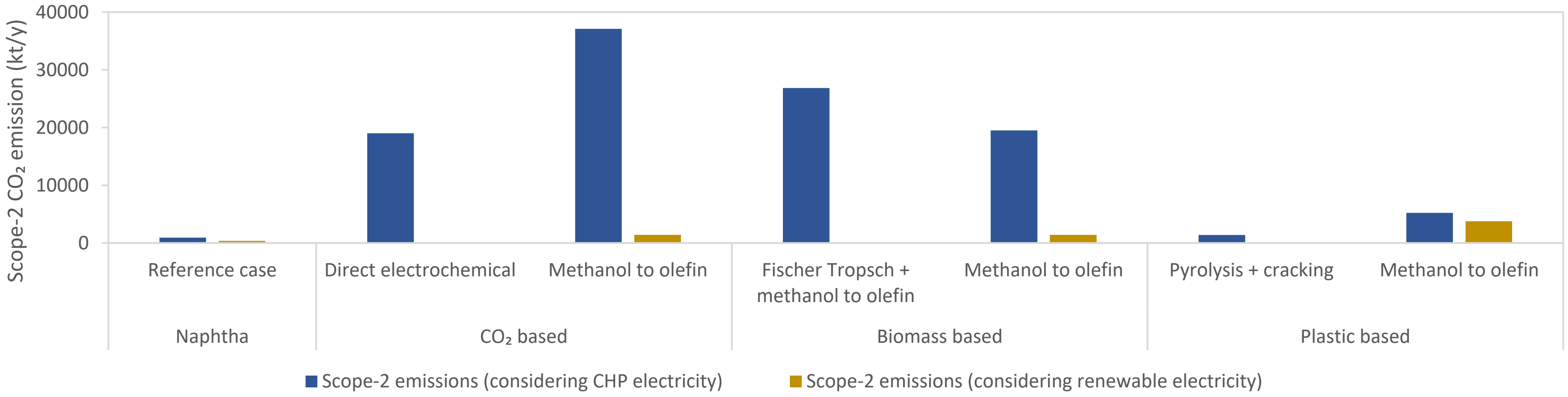

Figure 9. Scope-2 CO_2 emission of different ACS-based technologies for 900 kt/y ethylene production

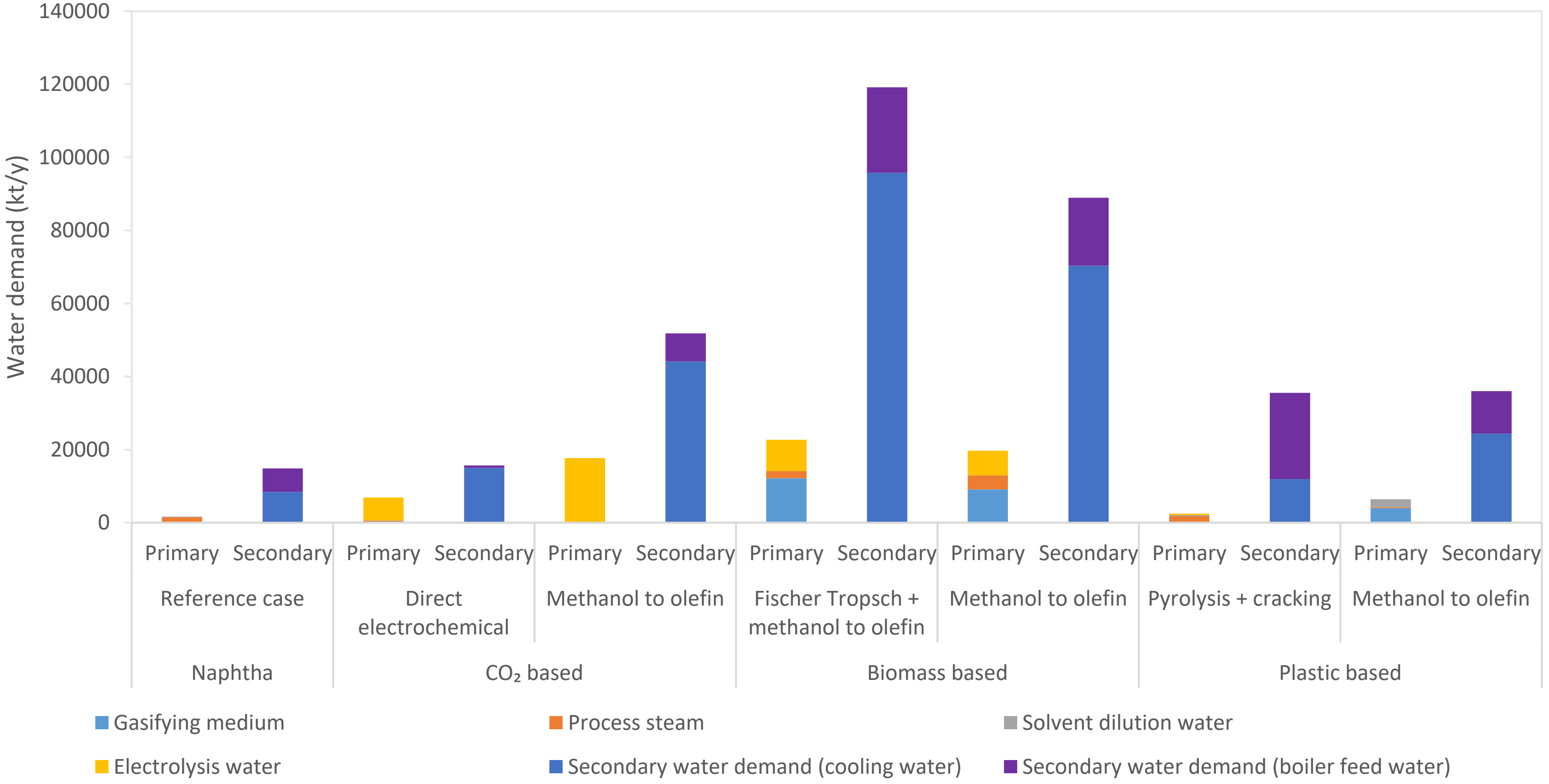

Figure 10. Primary and secondary water demand of different ACS-based technologies for 900 kt/y ethylene production

3.3 Scenario Analysis

The OPEX and CAPEX analysis of the ACS-based processes, shows that the major factors contributing towards the OPEX and CAPEX of these processes are: electrolyser cost, utility cost and raw material cost (as explained in section 3.1 and seen in SI Figure S25 to Figure S38). Based on this analysis, a scenario analysis is conducted for the following parameters: feedstock price, solvent price, operating voltage, electrolyser cost, electrolyser life, electricity price and ROI (as given in Table 4).

The scenario analysis for CO_2 based direct electrochemical process shows that the technology is highly fluctuating to electrolyser cost, electrolyser life and electricity price for the boundary conditions assumed (Figure 11 (a)). For the CO_2 based direct electrochemical process (as observed in Figure S52 SI), in the worst-case scenario, the ethylene MSP can be as high as 23650 EUR/t. And in the best-case scenario, the ethylene MSP can be as low as 1204 EUR/t. The CO_2 based methanol to olefin process is also most fluctuating to electricity price for the boundary conditions assumed (as seen in Figure 11 (b)) and shows an ethylene MSP between 1436 EUR/t to 10769 EUR/t in the respective best- and worst-case scenarios (as seen in SI Figure S53).

In the case of biomass-based Fischer Tropsch + methanol to olefin process, it is observed as seen in Figure 11 (c), that the process is most affected not only to electricity price but also to biomass feedstock price. For the best-case scenario, the ethylene MSP is as low as 667 EUR/t and for the worst-case scenario, the ethylene MSP is 7041 EUR/t for the biomass-based Fischer Tropsch + methanol to olefin process (as shown in SI Figure S54). In the case of biomass the methanol to olefin route, Figure 11 (d), the process is most fluctuating to electricity price, syngas cleaning solvent price and biomass feedstock price. The analysis shows that the biomass-based methanol to olefin process does not have high variability for ethylene MSP (i.e., 1586 EUR/t to 8675 EUR/t in SI Figure S55), as seen in CO_2 based processes.

For plastic based pyrolysis process (Figure 11 (e)), the process is highly influenced by the waste plastic price for the boundary conditions. The scenario analysis (Figure S56 and Figure S57 in SI) shows that the plastic based pyrolysis process has the least variation of 632 EUR/t to 1445 EUR/t, compared to the other technologies and potentially could have an MSP comparable to that of the current ethylene MSP (1075 EUR/t). In the case of plastic based methanol to olefin process, Figure 11 (f), the process is most fluctuating to the syngas cleaning solvent price and plastic feedstock price. The analysis shows that the plastic based methanol to olefin process has an MSP variation between 1263 EUR/t to 3080 EUR/t (as shown in Figure S58 in SI).

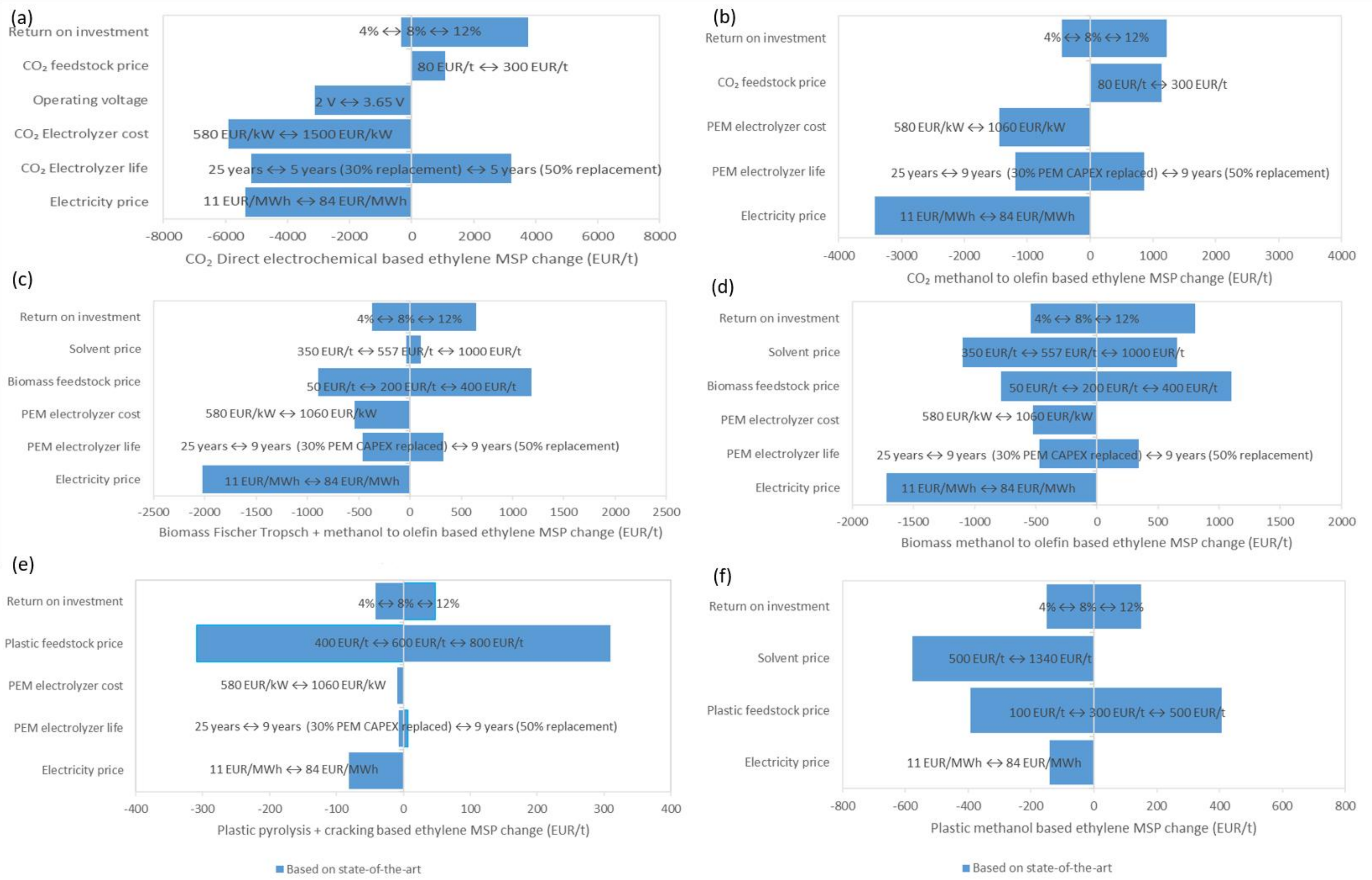

Figure 11. (a) Scenario analysis of CO₂ direct electrochemical based ethylene MSP, (b) Scenario analysis of CO₂ methanol based ethylene MSP, (c) Scenario analysis of biomass Fischer Tropsch + methanol based ethylene MSP, (d) Scenario analysis of biomass methanol based ethylene MSP, (e) Scenario analysis of plastic pyrolysis+ cracking based ethylene MSP, (f) Scenario analysis of plastic methanol based ethylene MSP

4 Conclusion

Defossilising the production of high-volume petrochemicals like ethylene will be vital to reducing the carbon footprint of our society and meet the ambitious CO_2 emissions targets needed to mitigate climate change. However, changing feedstock in a highly interconnected existing cluster can have unintended cascading effects on upstream supply-chains, downstream units and energy islands. The results indicate that in the case of ethylene, it won't be a plug-and-play situation, as the ACS-based processes have highly different product distribution, energy needs and waste generation. The process that has the most similar product distribution and the least impact in the existing petrochemical cluster is the waste plastic pyrolysis process. A significant challenge for other ACS-based technologies is the sizeable amount of renewable electricity at cheap price that will be needed for the hydrogen production required in the routes. The results at cluster level show that for the existing cluster it will not be easy to replace the naphtha cracker with ACS-based technologies due to limitation in area and additional requirements (like electricity supply, water supply); as the ACS-based processes need around 5 to 10 times higher area, electricity or water.

The chapter also highlights the importance of studying ACS technologies in the context of multiple products in highly symbiotic industrial clusters, as defossilising ethylene can create shifting of burden to outside the cluster and may result in a net increase of the fossil fuel consumption. The unintended major environmental consequences of defossilising ethylene production were the large water consumption and CO_2 emissions (scope-1 and scope-2), which could nullify the purpose of defossilisation chemical building blocks. The CO_2 emissions analysis shows that ACS-based technologies should be deployed in tandem with renewable energy-based utilities for the system to be low-carbon. Future studies should look into the potential of recycling wastewater, valorising waste and integration of renewable energy for heating needs in ACS-based processes to make it more environmentally appealing. However, to achieve cost competitiveness with existing fossil-based counterparts at current conditions, availability of low-priced renewable energy, feedstocks as well as efficient and durable electrolysers are critical.

Similar to olefins, aromatics are key building blocks in a chemical cluster and it is important to understand the impact of defossilising aromatics along with olefins to get a comprehensive view. This is addressed in the next chapter of this thesis.

5. Ripple effects of defossilising aromatics production in petrochemical clusters

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This chapter is based on the manuscript Manalal J. T., Pérez-Fortes M., Ramirez A., Ripple effects of defossilising aromatics production in petrochemical clusters (submitted)

Chapter specific nomenclature & symbols

Nomenclature

ACS	Alternative carbon source	MTA	Methanol to aromatics
BFW	Boiler feed water	MTBE	Methyl tert-butyl ether
BSG	Biomass steam gasification	NCR	Naphtha catalytic reformer
BTX	Benzene, toluene and xylene	OPEX	Operational expenditure
C2M	Carbon dioxide to methanol	PEM	Proton exchange membrane
CAPEX	Capital expenditure	PET	Poly Ethylene terephthalate
CBB	Chemical building block	PFD	Process flow diagram
CHP	Combined heat and power	PGME	Propylene glycol methyl ether
CW	Cooling water	PMDI	Polymeric methylene diphenyl isocyanate
EB	Ethyl benzene	PO	Propylene oxide
EDC	Ethylene dichloride	PoR	Port of Rotterdam
EDTA	Ethylene diamine tetra acetic acid	PSG	Plastic steam gasification
EO	Ethylene oxide	PTA	Purified terephthalic acid
HHPS	High-high pressure steam	PVC	Polyvinyl chloride
HPS	High pressure steam	RME	Rapeseed methyl ester
HT	High temperature	ROI	Return on investment
IPA	Iso-propyl alcohol	S2M	Syngas to methanol
KPI	Key performance indicator	SM	Styrene monomer
LLPS	Low-low pressure steam	TBA	Tert-butyl alcohol
LPS	Low pressure steam	TDB	Toluene disproportionation to benzene
MDA	Methylenedianiline	TEE	Techno-economic-environmental
MDI	Methylene diphenyl diisocyanate	TRL	Technology readiness level
MPS	Medium pressure steam	WE	Water electrolysis
MSP	Minimum selling price	XI	Xylene isomerisation

Abstract

More than 50% of the feedstock carbon in petrochemical clusters stems from the production of high-volume chemicals like benzene and p-xylene. These are typically produced from fossil-based carbon sources within highly integrated systems, where mass and energy flows are tightly interconnected. Transitioning to alternative carbon sources (ACS) can significantly disrupt these interactions, an aspect that is overlooked in existing literature. This chapter addresses this knowledge gap by evaluating the impact of replacing fossil-based benzene production with ACS-based routes using CO_2, biomass, and plastic waste. It explicitly evaluates performance at both the process and cluster levels by assessing changes in mass, energy, prices, CO_2 emissions, and water demand. The results show that due to differences in product distribution, energy requirements, and waste generation, ACS-based processes can trigger unintended ripple effects across downstream units, utility providers, and waste treatment plants. Among the evaluated options, plastic waste-based benzene emerges as the most competitive technology under current market conditions, with the lowest impact at the cluster level. However, its viability depends on the availability of plastic waste, which is a constraint given current recycling rates. Further improvements in waste valorisation and integrating renewable heat are essential to improve the environmental performance of this technology.

1. Introduction

The petrochemical industry is a hard-to-abate sector due to its deep reliance on the oil and gas industry for both feedstock and energy. Its complexity is further amplified by a highly interconnected network of mass and energy flows, driven by the wide array of products generated during production. Feedstocks like naphtha, pygas or reformate, are first converted to chemical building blocks like olefins (ethylene, propylene) and aromatics (benzene, p-xylene), which are then further processed, through multiple interconnected processes, into downstream derivatives. 88% of the carbon embedded in chemical building blocks and their downstream derivatives originates from fossil sources [3]. In the Port of Rotterdam, for example, aromatic products like benzene and p-xylene account for over 50% of the embedded carbon as shown in Figure 1 [119]. This highlights the potential of defossilising aromatics production to reduce fossil feedstock use across the entire cluster. Despite this potential, the systemic impact of defossilising aromatics production remains largely underexplored in literature.

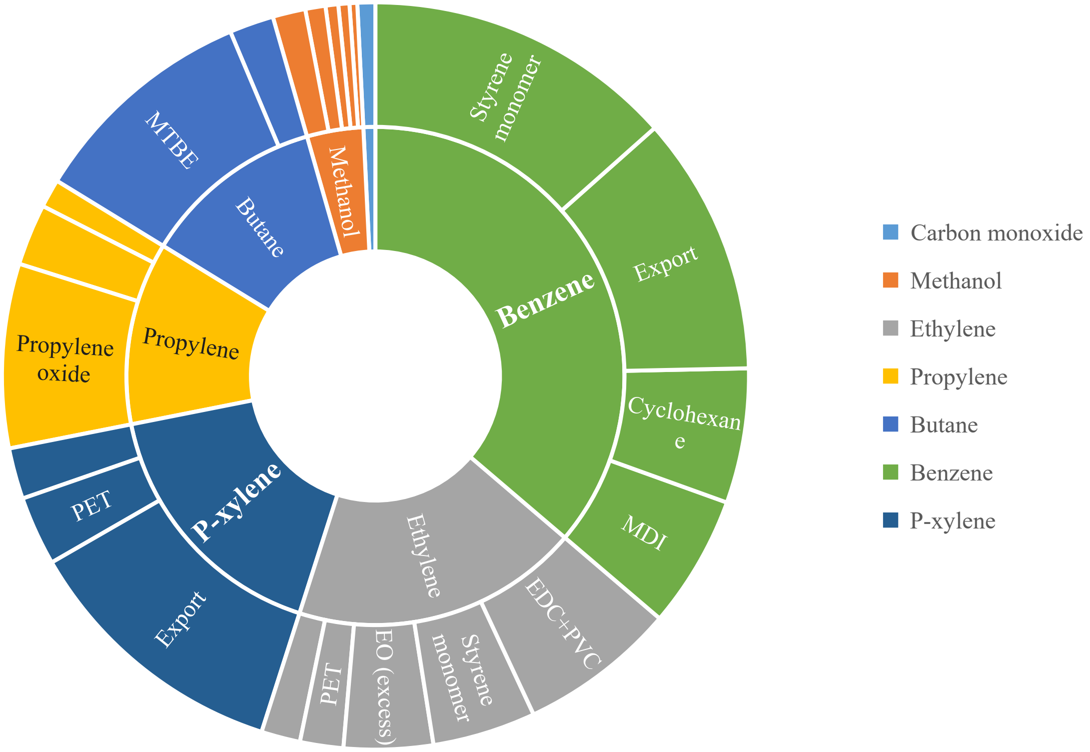

Figure 1: Distribution of embedded carbon in chemical products in the Port of Rotterdam (calculated based on data from Port of Rotterdam, 2016).

Existing studies on the use of alternative carbon sources (ACS) such as CO_2, biomass, and waste plastic for aromatics production are limited, particularly in terms of techno-economic analysis. For instance, Bazzanella et al[42] compared conventional fossil-based routes for the production of benzene, toluene and xylene (BTX) with methanol to aromatics (MTA) processes that depart from CO_2 and biomass. Their findings showed that MTA routes require around 25 times more electricity than traditional naphtha crackers mainly due to the high energy demand for hydrogen production. Economically, the production cost of MTA-based BTX was found to be three times more expensive than the fossil-based alternatives. Further studies by D. Zhang et al., (2019) and Jiang et al., (2020) also evaluated MTA processes. D. Zhang et al., (2019) highlighted the low selectivity for benzene, with higher yields of toluene, p-xylene, and light gases. Note that 90% of the total production cost was attributed to methanol synthesis. Jiang et al., (2020) compared MTA with naphtha catalytic reforming

(NCR), concluding that MTA was 1.5 times more expensive. Both studies identified low benzene yields in the MTA process as a key challenge. However, by-products like toluene and xylene can be converted to benzene via mature industrial processes such as toluene disproportion and xylene isomerisation reactions [122]. The techno-economic implication of integrating these conversion steps remains, to the best of our knowledge, unaddressed in the literature.

The studies listed above focused on assessing CO_2 or biomass as feedstocks, neglecting plastic waste as a carbon source and overlooking the potential cascading impacts of integrating ACS within highly interconnected petrochemical clusters. In fact, we could not find any publication in open literature that comprehensively studied the techno-economic impacts of changing carbon feedstocks to produce aromatics at both the process and cluster levels. This study aims to address these knowledge gaps by evaluating the techno-economic and environmental (TEE) impacts of using ACS feedstocks for aromatic production in an existing petrochemical cluster.

2. Methodology

To evaluate the TEE impacts of defossilising aromatics production within an existing petrochemical cluster, a reference case was developed based on the industrial cluster in the Port of Rotterdam, the Netherlands. Potential ACS-based processes were identified using the screening methodology developed in Chapter 2 and modelled using Aspen plus, scaled to match the output capacities of the reference case.[79] TEE impacts were evaluated using selected key performance indicators (KPIs), first at the process level. These results were then used to study the impacts at cluster-level. A detailed description of the methodology follows.

2.1 Reference case: the fossil-based aromatic cluster

This study draws on material, energy, and economic data from an in-house reference petrochemical cluster, modelled in Aspen Plus v12 and described in Tan et al., (2024). The model of the industrial cluster comprises 57 chemical processes and associated utility islands. For this analysis, we focus on the aromatic subcluster, as depicted in Figure 2, where blue and violet lines represent the benzene and xylene value-chains, respectively.

The aromatic process in the reference case (Figure 3) includes pre-treatment, BTX distillation, xylene isomerisation, and toluene disproportionation sections [122]. Fossil-based feedstocks like pygas, C7+ and reformate, contain aromatics or BTX components [123]. This mixture are first pre-treated using distillation and hydrotreatment to remove heavier hydrocarbons, sulphur and light gases [122]. The resulting BTX mixture undergoes complex separation, including extractive distillation, due to its azeotropic nature [122]. Xylenes from the distillation section are further separated into o-xylene, p-xylene, m-xylene and ethylbenzene. The m-xylene/ethylbenzene stream is processed in an isomerisation unit (400 °C, 14 bar) to convert m-xylene to p-xylene and hydrogenate ethylbenzene to benzene [122,123]. Toluene from the BTX unit is sent to a disproportionation unit (400 °C, 30 bar) to produce benzene and p-xylene [122,123].

The main products from the aromatics plant are benzene, p-xylene and o-xylene. Figure 3 shows a simplified block flow diagram, the detailed process flow diagram (PFD) is provided in SI Figure S1. Figure 4 shows the utility island of the reference aromatics plant, which includes electricity, heating and cooling flows, its downstream units, the refinery gas boiler, and a combined heat and power (CHP) plant. The detailed energy and mass balances for the different processes is provided in the Zenodo repository (links provided in SI).

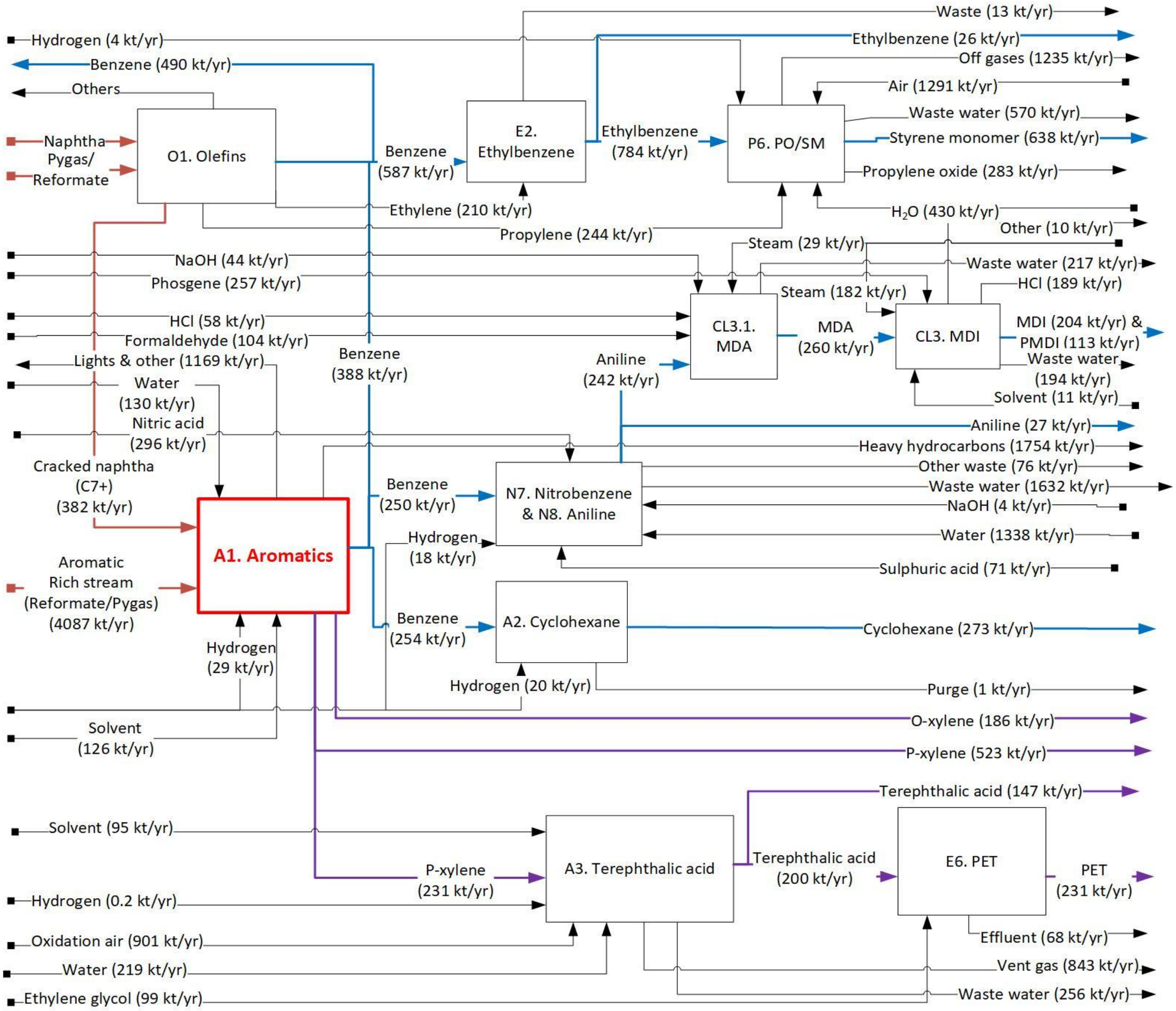

Figure 2: Aromatic cluster in te PoR with benzene and p-xylene value-chains in blue and violet. In brackets the annual production capacities. (Abbreviations: PO- Propylene oxide, SM- Styrene monomer, MDA- Methylenedianiline, MDI- Methylene diphenyl diisocyanate, PMDI- Polymeric methylene diphenyl isocyanate, PET- Polyethylene terephthalate).

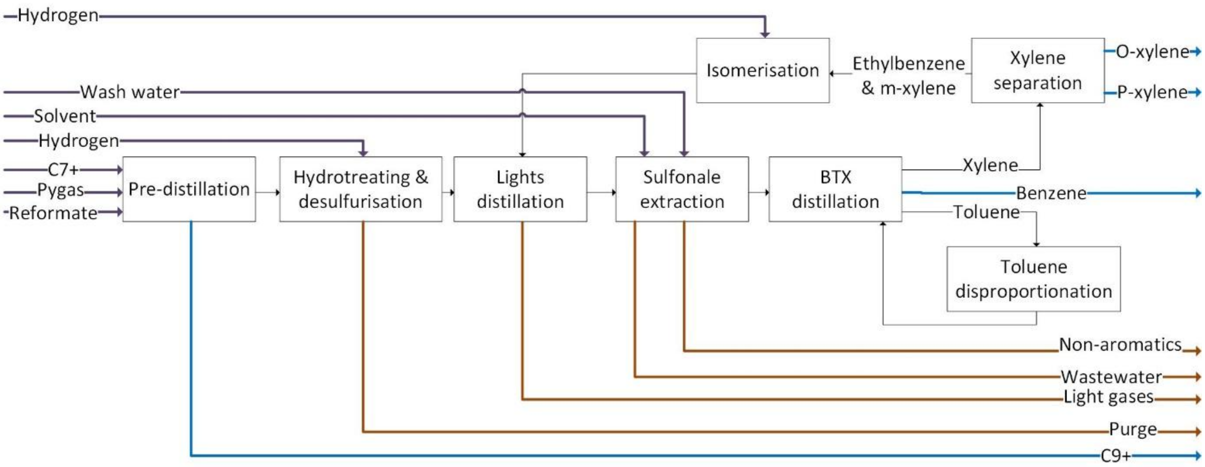

Figure 3: aromatic production process in the reference case (Abbreviation: BTX- benzene, toluene and xylene)

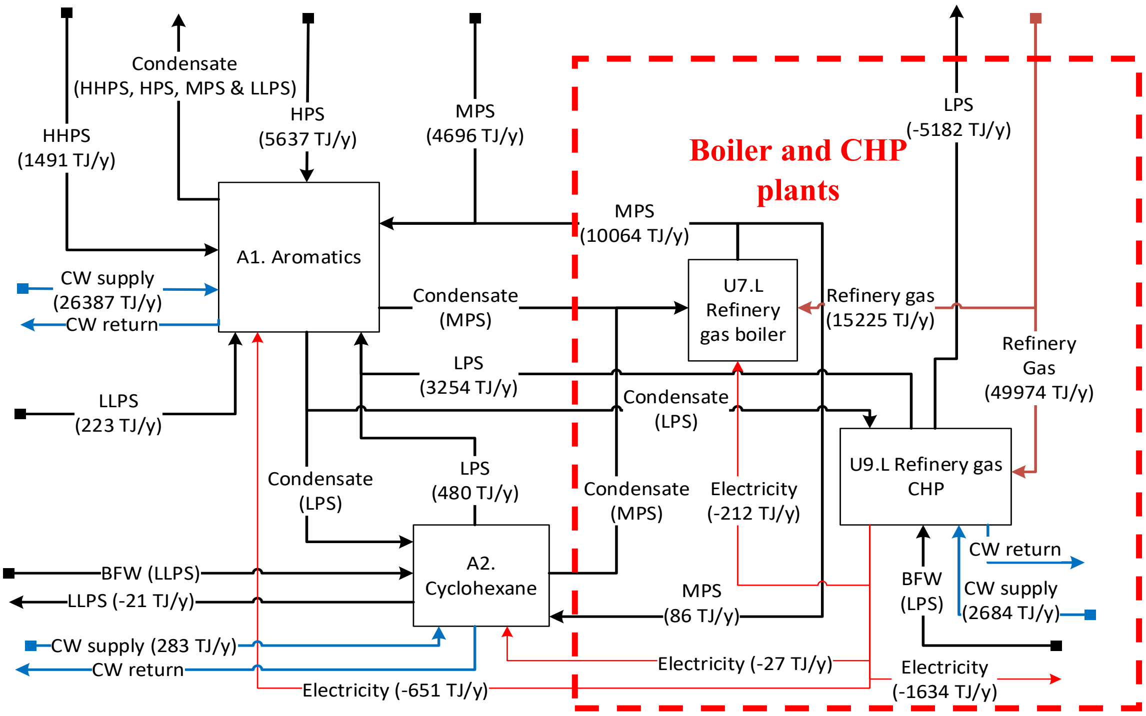

Figure 4: Energy utilities in the reference case to produce aromatics (Note: The negative sign refers to heat or electricity generated in the process, while a positive sign refers to heat or electricity required by the process)

2.2 Ex-ante ACS process modelling

Three ACS benzene production routes (Table 1) were selected for this study based on the technology screening methodology developed in Chapter 2 and Chapter 3. These ACS-based routes were modelled using Aspen Plus and Aspen Economic Analyzer v12. The detailed data and parameters used in each model is provided in the Zenodo repository (links provided in SI).

Each route was designed to produce a benzene at 99.5 wt% purity, with a production capacity of approximately 500 kt/y. Although the total benzene demand in the cluster is 1,000 kt/year, a 500 kt/year capacity was chosen to ensure that equipment sizes remained within commercially available limits for methanol production and gasification technologies [124–126]. To meet the total benzene demand, it was assumed that two parallel ACS units would be required for each route. A brief description of each route is provided below.

Table 1: Selected ACS-based technologies for aromatics production.

Alternative Carbon Source routes		
CO_2-based route	**Biomass-based route**	**Plastic waste-based route**
Water electrolysis + CO_2 hydrogenation to methanol + methanol to aromatics + toluene disproportionation to benzene + xylene isomerisation	Water electrolysis + biomass steam gasification to syngas + syngas to methanol* and Water electrolysis + CO_2 hydrogenation to methanol * + methanol to aromatics + toluene disproportionation to benzene + xylene isomerisation	Plastic steam gasification to syngas + syngas to methanol + methanol to aromatics + toluene disproportionation to benzene + xylene isomerisation

*: *in the biomass route, these are parallel units, see section 2.2.2*

2.2.1 CO_2-based route

Pure CO_2 (see Appendix B Table B1) was indirectly converted to benzene via a two-step process: CO_2 hydrogenation to methanol and methanol to aromatics (Figure 5). In the first step, CO_2 was hydrogenated to methanol (C2M) in a tubular reactor (69 bar, 255 °C), using a Cu-ZnO-Al_2O_3 catalyst [124,127]. Hydrogen was obtained from water electrolysis (WE) [128], maintaining a H_2/CO_2 ratio of 3 in the feed gas to the methanol reactor [124]. Due to the low single-pass conversion of CO_2 (20% to 30%) reported in the literature [129], unconverted gases were recycled with the purge stream, which ranged from 5% to 10%. The resulting methanol was purified (99.9 wt% pure) via distillation to remove light gases and water. In the second step, methanol was fed into a fluidised bed MTA reactor (60 bar, 450 °C) [130–132], producing benzene along with by-products like methane, ethane, propylene, propane, C4's, toluene, xylene (see SI Table S9). To increase the benzene yield, toluene and xylene, were further processed using a toluene disproportionation to benzene (TDB) reactor and a xylene isomerisation (XI) unit, modelled in line with the reference case (Section 2.1). The final product mixture was separated into high-purity products using a series of advanced separation steps (dehydration, cryogenic distillation, extractive distillation). The detailed PFD of the route is shown in SI Figures S2, S3 and S4. The detailed data and parameters used for the simulation is provided in Zenodo repository (links provided in SI).

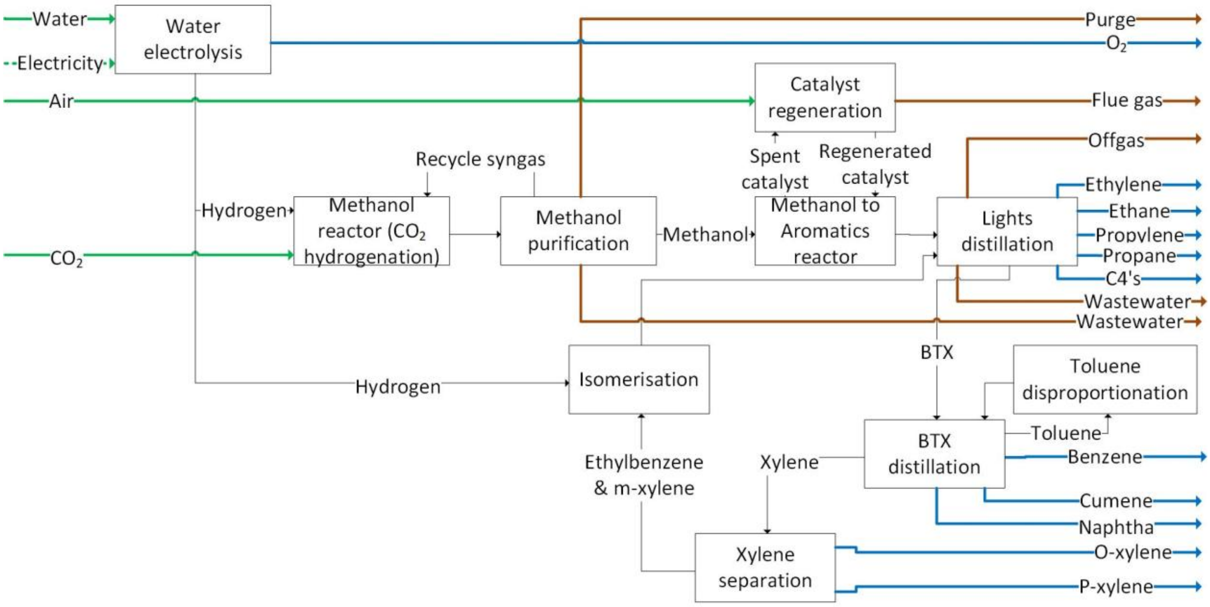

Figure 5: CO_2-based route in this study (Abbreviations: BTX- benzene, toluene and xylene).

2.2.2 Biomass-based route

Lignocellulosic biomass residues (composition in Appendix B Table B2) can be converted to benzene via a three-step process: biomass steam gasification (BSG), syngas to methanol (S2M), and MTA (see Figure 6). Steam gasification occurs in a fluidised bed reactor at 800 °C to 900 °C and near atmospheric pressure, using olivine as the bed material [133]. The resulting raw syngas is cleaned to remove impurities such as entrained catalyst, water, tar, and acid gases. The cleaned syngas has a H_2-CO_2/CO+ CO_2 ratio of 0.7, which is below the required threshold (>2) for methanol synthesis [124]. To adjust the ratio, excess CO_2 was removed via acid gas removal, yielding a CO-rich syngas suitable for methanol production.

Methanol synthesis is performed in a fixed-bed reactor at 69 bar and 255 °C, over a Cu-ZnO-Al_2O_3-based catalyst [124,127], as described in the CO_2-based route. The CO_2-rich gas from the acid gas removal unit is also used for methanol production after further desulfurisation and hydrogenation with additional hydrogen supplied via water electrolysis [128]. The downstream MTA, TDB, and xylene isomerisation sections were modelled as described in the previous section. The final product mixture is purified into

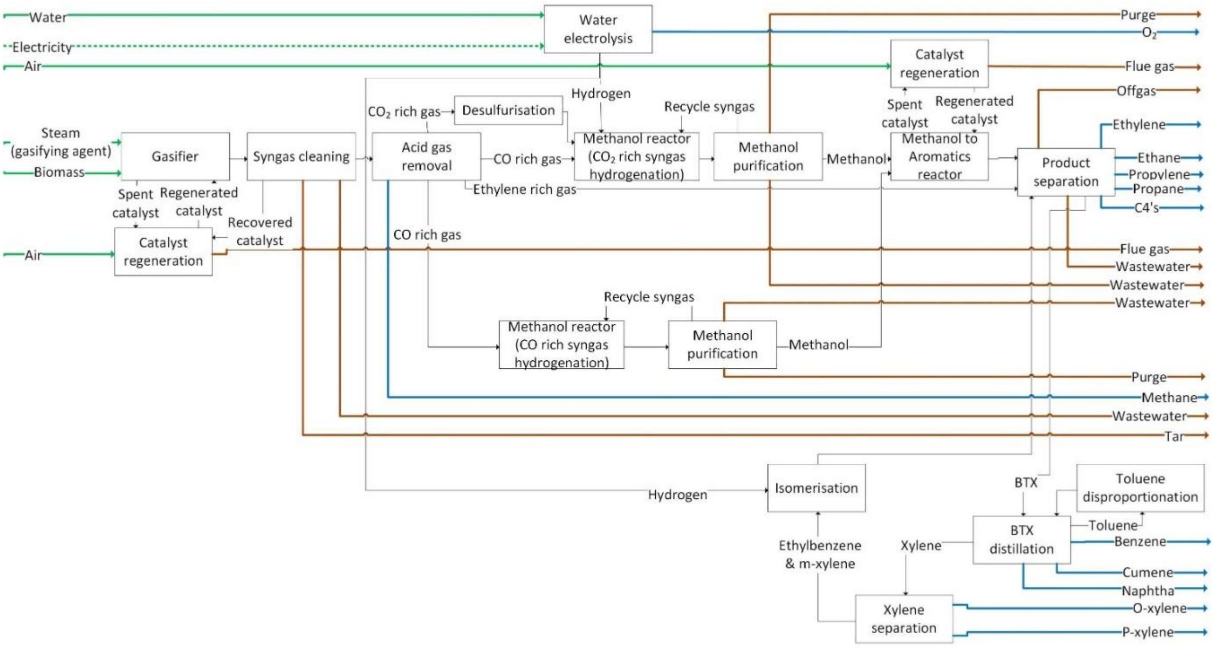

Figure 6: Biomass-based route in this study (Abbreviations: BTX- Benzene, toluene and xylene)

high-purity products using a combination of dehydration, cryogenic distillation, and extractive distillation. Detailed PFD of the route is shown in SI Figures S3, S4 and S5. The detailed data and parameters used for the simulation is provided in Zenodo repository (links provided in SI).

2.2.3 Plastic waste-based route

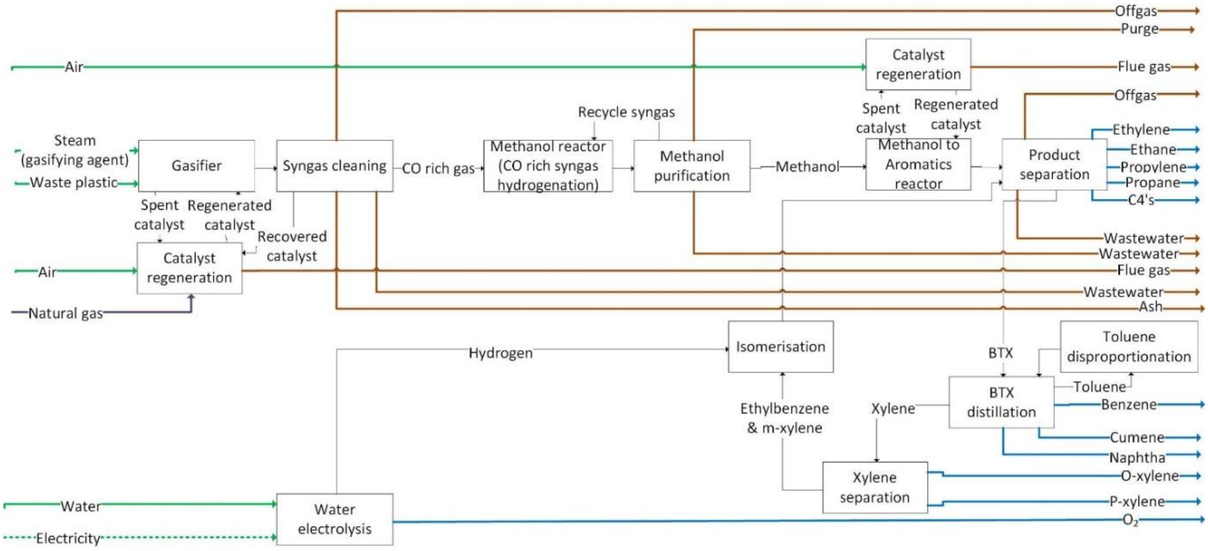

Figure 7: Plastic waste-based route in this study (Abbreviations: BTX- Benzene, toluene and xylene)

Unsorted plastic waste (composition in Appendix B Table B3 and Table B4) is converted to benzene via steam gasification followed by the MTA route as shown in Figure 7. Steam gasification occurred in a fluidised bed reactor at 800 °C to 1000 °C near atmospheric pressure, using sand as the bed material [134,135]. The resulting raw syngas is cleaned to remove impurities (entrained catalyst, water, tar, and acid gases). The clean syngas was then converted to methanol in a tubular reactor at 69 bar and 255 °(E. Lücking & de Jong, 2017; Ott et al., 2012)[124,127]. Unlike the biomass and CO_2 routes, this process does not require additional hydrogen or acid gas removal as the syngas had a $H_2/(CO+CO_2)$ ratio above 2.

The downstream MTA, TDB, and xylene isomerisation sections were modelled as described in the CO_2-based route. Detailed PFDs are provided in SI Figures S3, S4 and S6. The detailed data and parameters used for the simulation is provided in Zenodo repository (links provided in SI).

2.3 Process and cluster level impacts

The ACS-based and fossil-based processes for aromatics production were evaluated using the key performance indicators (KPI's) shown in Table 2. The process level KPI's were based on process complexity, performance, efficiencies, energy needs, economics, CO_2 emissions and water demand. At the cluster level, KPIs related to mass flows, energy consumption, and product pricing were used to assess the systemic impacts of integrating ACS-based routes. These indicators help characterise the interdependencies between processes within the cluster and quantify potential ripple effects.

Table 2: Techno-economic and environmental KPI's used in this study.

Assessment level	**Key performance Indicators**		
	Technical	**Economic**	**Environmental**
Process level	• Process complexity (process temperature range, process pressure range, single pass conversion, bare equipment area) • Product yields and product purity • Heating, cooling and electricity (utility needs)	• CAPEX • OPEX • Minimum selling price (MSP)	• Scope-1 CO_2 emissions • Primary water demand • Carbon utilisation efficiency (CUE)
Cluster level	Import or export dependency impacts (feed, products, utility): • change in mass flows* • change in energy flows*	• CAPEX • change in MSP *	• Scope-1 and scope-2 CO_2 emissions • Primary and secondary water demand

**: Change with respect to the reference case*

A heat integration strategy, similar to the one described in Tan et al., (2024), was applied to both the reference and ACS-based processes. This involved heating or cooling streams stepwise using multiple utilities, including refrigerants (R50, R1150, R134a), steam at different qualities (low-low pressure steam (LLPS), low pressure steam (LPS), medium pressure steam (MPS), high pressure steam (HPS), high-high pressure steam (HHPS)), cooling water, natural gas and electricity. Utility characteristics are detailed in Table 3 of Chapter 4.

Capital expenditure (CAPEX), operational expenditure (OPEX), and the minimum selling price (MSP) were calculated using assumptions from SI Table S6 to S8, and Equations S3-S4, aligned with Chapter 4. Changes in MSP for downstream products were used to assess cascading impacts on the prices resulting from changes in benzene production cost, following Chapter 2 (see SI Equation S3).[79] Scope-2 emissions were estimated using a CO_2 intensity of 110 ktonne CO_2/PJ for electricity and 106 ktonne CO_2/PJ for steam, assuming the same CHP plants and boilers as in the reference case (see SI Table S4 for refinery gas composition). Scope-3 emissions were excluded, as the analyses focused on gate-to-gate cluster level impacts.

Water demand was assessed in two categories: primary water demand was calculated using total process water; and secondary water demand from make-up water for boiler feed water (25% make-up [117]) and cooling water (2% make-up [116]). The carbon utilisation efficiency (CUE) was calculated based on Chapter 2.[79] It is defined as the ratio of carbon in the products to the amount of carbon in the feedstock (see SI Equation S1).

Three ACS-based models (section 2.2) were developed for an industrial scale capacity of 500 kt/y benzene production. Each ACS-based route was assessed individually by introducing one ACS process at the time (requiring two plants to meet the 1000 kt/y benzene demand) using material and energy flow analysis with assumption as outlined in Chapter 4 (Methodology). The ACS-based processes were first analysed at the process level, and then at the cluster, using the KPI's described in Table 2.

2.4 Scenario analysis

A scenario analysis was done to explore the impact of the data inputs and modelling assumptions on the calculated MSP of benzene. For simplicity, only the uncertainty of benzene price is analysed and discussed, as the percentage MSP change for p-xylene is the same as that for benzene due to the revenue allocation technique used in Chapter 2.[79] The main contributing factors to MSP were identified and varied within the upper and lower limit values found in literature (see Table 3).

Table 3: Variables assessed in the scenario analysis (Abbreviations: PEM: proton exchange membrane, RME: Rapeseed methyl ester, EDTA: ethylene diamine tetra acetic acid)

Variables	Upper limit	Base-value	Lower limit
Return on investment (%)	12	8	4
Food grade CO_2 price (EUR/t)	300	80	80
Biomass pellet price (EUR/t)	400	200	50
Unsorted waste plastic price (EUR/t)	500	300	100
RME solvent price (EUR/t)	1000	557	350
Operating life of a PEM water electrolyser (years)	25	9 (with 30% component replacement)	9 (with 50% component replacement)
Cost of a PEM water electrolyser (EUR/kW)	1060	1060	580
Electricity price (EUR/MWh)	84	84	11
EDTA solvent price (EUR/t)	1340	1340	500

3. Results and discussion

3.1 Process level impacts of using ACS in benzene production

Defossilising benzene production using ACS feedstocks leads to significant changes in mass flows of raw materials, products and waste streams, as shown in Table 4. These shifts are mainly driven by lower benzene yields in the MTA process, reduced carbon utilisation efficiency (CUE), and increased waste generation in the ACS-based routes. Sankey diagrams (SI Figures S7–S10) illustrate these altered flow patterns. The lower carbon efficiency in ACS-based processes is attributed to low single-pass syngas conversions, high purge requirements (5% to 10%), and side reactions, including tar and char formation, in the gasification reactors. Although the use of toluene disproportionation and xylene isomerisation reactions improve the benzene yield in the MTA section, from 2% to 6% relative to methanol input, the overall benzene yield from ACS feedstock (i.e., ratio of mass flow of benzene to mass flow of ACS feedstock) remains between 3% and 8%, which is still substantially lower than the 20% benzene yield in the reference case.

Table 4: Annual mass flows at process level for the different ACS-based route for benzene production

Mass flows		**Fossil-based Reference case**	**CO_2-based route**	**Biomass-based route**	**Plastic waste-based route**
Raw materials (kt/y)	Carbon feedstock	4366 (from reformate, pygas and C7+)	35200 (Food grade CO_2)	37840 (Wood pellets)	13640 (Municipal plastic waste)
	Water and Steam	130	43472	39072	9988
	Other feedstocks	28	0	0	0
Products (kt/y)	Methane or Lights	1140	12066	6434	2298
	Methanol	-	264	616	352
	Ethane	-	390	390	390
	Ethylene	-	40	40	40
	Propane	-	1282	1282	1282
	Propylene	-	136	136	136
	C4 mixture	-	1842	1842	1842
	Benzene	853	1070	1070	1070
	Cumene	-	480	480	480
	P-xylene	730	1944	1944	1944
	O-xylene	182	10	10	10
	C7+ and Naphtha	687	64	64	64
	Non-aromatics and Tar	924	-	924	2728
	Oxygen	-	38598	14970	274
Waste (kt/y)	Wastewater	130	20486	39406	10146
	Hydrocarbon waste	38	0	0	0
	Purge and off-gas	41	12066	4498	2298
	Char and ash	0	0	6292	572
	Tar	0	0	924	2728
Process carbon utilisation efficiency (CUE)		95%	66%	47%	64%
Benzene yield (Benzene to carbon feedstock mass %)		20%	3%	3%	8%

A significant change is also observed in product distribution. In the reference case, benzene and p-xylene are produced in nearly equal proportions. However, in the MTA-based processes, the ratio shifts to a 1:2 ratio (see SI Table S10). This results in a significant increase in p-xylene production when using

ACS-based routes. As shown in Table 4, the production of by-product oxygen also varies across the routes. The CO_2-based process generates c.a. 38,600 kt/year of oxygen, while the biomass-based process produces around 15,000 kt/year. In contrast, the plastic-based process generates only about 270 kt/year of oxygen, as its syngas already meets the required $H_2/(CO+CO_2)$ ratio for methanol synthesis, reducing the need for external hydrogen and associated oxygen production.

Although benzene purity is larger than 99.5% in all cases, the impurity profiles differ. In the reference case, impurities include toluene and nitrogen, while in the ACS-based processes trace impurities such as hydrogen, ethane, butane, butene, and toluene are present at ppm level (see SI Table S12). These differences may affect the downstream aromatic value chains. A detailed assessment of these aspects is beyond the scope of this chapter and warrants further investigation.

The ACS-based processes also show significant differences in electricity, heating and cooling requirements or production. As shown in Table 5, the reference case relies mainly on heat as its main energy input and does not produce excess steam, largely due to the high thermal requirements of complex distillation processes. In contrast, the CO_2 and biomass-based ACS processes, despite requiring similar distillation steps, are net heat producers. This is due to the exothermic nature of the MTA process and integration of waste-to-energy recovery units. The plastic waste-based MTA process, however, requires c.a 55 PJ of LP steam and 110 PJ of high-temperature utilities (above 350 °C). This heat demand is due to a lower off-gas generation (2298 kt/y) compared to 12066 kt/y for the CO_2 abased process and 4498 kt/y for the biomass-based processes. Note that the CO_2 and biomass-based processes achieve energy self-sufficiency through the combustion of off-gases, leading to low carbon utilisation efficiencies. A comparison of gasification heat requirements shows that the biomass-based gasification process needs more energy (~215 MJ heat/kg benzene produced) than the plastic-based process (23 MJ heat/kg benzene produced). However, the biomass-based process benefits from the production of large quantities of off-gases, which can be combusted to recover heat.

All ACS-based benzene production routes require substantially more electricity compared to the reference case. A significant share of this electricity is for hydrogen production, except in the case of plastic waste. For instance, the CO_2 MTA route requires around 1000 times more electricity than the reference case due to the high hydrogen demand (2437 kt/y). The biomass MTA process requires lower electricity than the CO_2 MTA route for hydrogen production, as it only needs 941 kt/y hydrogen. For the plastic MTA route, only 15% of the total electricity required is for hydrogen production, while the majority (65%) is needed mainly for syngas pressurisation and recycling.

Table 5: Utilities at for c.a 1000 kt/y benzene production. A negative sign refers to energy produced by the system, while a positive sign refers to energy required (Abbreviations: LLPS: Low-low pressure steam, LPS: Low pressure steam, MPS: Medium pressure steam, HPS: High pressure steam, HHPS: High-high pressure steam, HT: High temperature)

Utilities		**Fossil-based Reference case**	**CO_2-based route**	**Biomass-based route**	**Plastic waste-based route**
Utility requirement or production (PJ/y)	Electricity	0.7	1152	585	51
	LLPS	0	-3	-4	-
	LPS	4	-107	-107	55
	MPS	15	-3	-41	-52
	HPS and HHPS	7	0	-141	-27
	HT utility	-	-	-	110
	Cooling water	26	310	510	158

All ACS-based routes have a higher maximum selling price (MSP) for benzene than the reference case (see Table 6). The CO_2-based benzene is the most expensive, followed by benzene derived from biomass and plastic waste. The MSP of benzene is two to seven times higher than in the reference case. This is due to the higher CAPEX investment ranging from 36 times to 200 times that of the reference case. A major share (42% to 54%) is due to methanol production (see SI Figures S12, S14, S16 and S18). OPEX is dominated by utility and feedstock costs (see SI Figures S13, S15, S17 and S19). In the CO_2-based route, utilities account for 62% of OPEX, while feedstocks contribute with only 7%. In contrast, the biomass-based route shows a more balanced distribution, with 36% of OPEX from utilities and 39% from feedstocks. In the plastic-based route, 69% of the OPEX is attributed to feedstock, and only 16% to utilities.

Table 6: Economic KPIs for each ACS-based route for c.a 1000 kt/y benzene production.

Economic indicators	**Fossil-based Reference case**	**CO_2-based route**	**Biomass-based route**	**Plastic waste-based route**
Benzene MSP (EUR/t)	1032	7657	5862	2528
CAPEX (Million EUR)	660	134124	96552	24084
OPEX (Million EUR/y)	3937	43502	39528	16429

In terms of revenue, the reference case accounts 95% of total revenue from the sale of light gases (like methane), benzene, C7+ and p-xylene. For the ACS-based processes, the source of revenue is more diversified with, propane, C4's, benzene and p-xylene as main contributors (see SI Table S13). The economic importance of benzene as the main product decreases in the ACS-based processes due to the lower selectivity of the MTA process for benzene production.

The ACS-based processes result in higher Scope-1 CO_2 emissions and primary water usage compared to the reference case (see Figures 8 and 9). The main sources of Scope-1 emissions are off-gas combustion, gasifier bed regeneration, and high-temperature heat. It is important to note that the origin of the emissions differs significantly between the reference and the ACS routes. In the reference, emissions originate from fossil-based feedstocks. ACS routes involve biogenic, waste, or captured CO_2. For biomass-based routes, the net carbon neutrality of biogenic emissions depends on the type of biomass and value chain. For plastic waste-based technologies, emissions are considered "free" of impact in life cycle analysis guidelines, although the applicability of this principle to waste-to-chemical concepts remains under debate. For CO_2-based technologies, the origin of CO_2 (fossil, biogenic, or atmospheric) significantly influences the assessment. Therefore, the impact of scope-1 emissions in Figure 8 on climate change can vary significantly depending on the feedstock.

Primary water demand in ACS-based processes is also considerably higher (Figure 9). This is due to water use for electrolysis, as solvent, washing agent, and gasifying medium. In the CO_2-based route, nearly all primary water is needed for hydrogen generation. For biomass and plastic-based routes, the major share of water is used as gasifying agent. Although the biomass-based route requires relatively less water for hydrogen production, its total water demand exceeds that of the CO_2-based route because a steam dilution ratio of 0.59 kg steam/kg biomass was used, based on GoBiGas gasification technology [118].

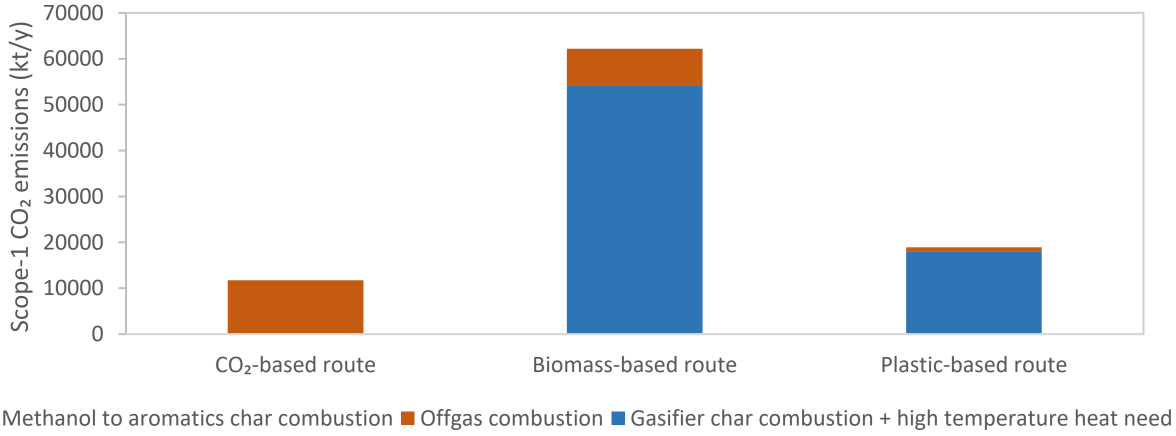

Figure 8: Scope-1 CO_2 emissions for the different ACS-based routes in this study for c.a 1000 kt/y benzene production.

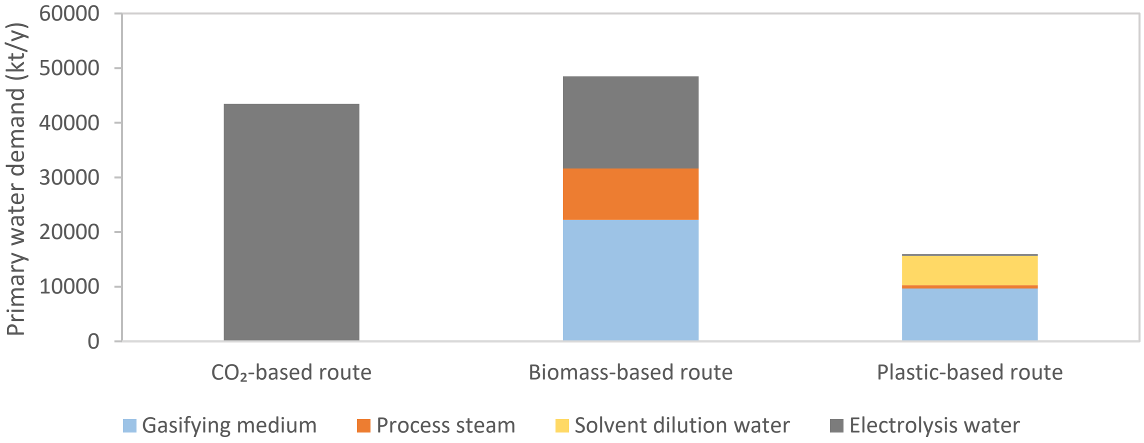

Figure 9: Primary water demand of different ACS-based processes for about 1000 kt/y benzene production (Note: The reference case primary water demand is not shown as the value 130 kt/y is comparatively negligible than the ACS based routes)

3.2 Cluster level impacts of defossilising the benzene production

The defossilisation of benzene production using ACS-based technologies results in significant changes in mass and energy flows at the cluster level as shown in Tables 7 and 8, SI Figures S20 to S22 (mass flows), and Figures S23 to S25 (energy flows). Notable changes are observed in mass streams like water, refinery imports, p-xylene, oxygen, wastewater and energy streams like LP steam, HT utility, and electricity. In all ACS-based cases, the import of fossil based chemical building blocks (CBB's) like propylene and C4's drops to zero (see SI Table S14). This is due to the production of light hydrocarbons (C_3- C_4 range) in the MTA process (see SI Table S9). As a result, defossilising aromatics production also triggers secondary effects on the availability and distribution of other CBBs within the cluster.

The ACS-based processes require significantly more feedstock per kilogram of benzene produced, up to 20 kg ACS feedstock compared to 3 kg pygas and reformate in the reference case. As explained in section 3.1, this is primarily due to the lower carbon utilisation efficiency of the ACS-based processes and the lower carbon content of CO_2 (~27 wt%) and biomass (~50 wt%) compared to fossil feedstocks.

The plastic waste-based process performs better. Requiring about 8 kg plastic per kg benzene, due to its higher carbon content (~81 wt%).

Mass flow analysis also reveals that ACS-based processes produce more propylene and p-xylene than the reference case, resulting in surplus output. In the reference case, the naphtha cracker is the only source of propylene and C4s. However, in the ACS-based cases, both the naphtha cracker and the MTA-based processes contribute to their production, leading to oversupply and multiple sources for these chemicals within the cluster. The results also point out a significant increase in wastewater (6 to 23 times higher than the reference case). Consequently, major infrastructure changes for wastewater treatment will be required when ACS-based technologies are introduced in the cluster.

Table 7: Comparison of mass flow changes at cluster level for the different ACS-based production processes.

Mass flow per unit of benzene (kg/kg)		**Fossil-based Reference case**	**CO_2-based route**	**Biomass-based route**	**Plastic waste-based route**
In	Naphtha (Refinery import)	1.9	1.7	1.7	1.7
	Pygas and reformate (Refinery import)	3.2	0.4	0.4	0.4
	Water	1.0	25.6	23.1	6.5
	Other input	0.2	0.1	0.1	0.1
	Propylene (Refinery import)	0.04	0.0	0.0	0.0
	C4's (Refinery import)	0.2	0.0	0.0	0.0
	Oxygen	0.4	0.0	0.0	0.2
	CO_2	0.0	20.0	0.0	0.0
	Biomass	0.0	0.0	21.5	0.0
	Plastic	0.0	0.0	0.0	7.8
Out	Ethylene (naphtha cracker)	0.6	0.5	0.5	0.5
	Propylene (naphtha cracker)	0.3	0.3	0.3	0.3
	C4's (naphtha cracker)	0.1	0.1	0.1	0.1
	Benzene (naphtha cracker)	0.4	0.4	0.4	0.4
	Ethylene (aromatics section)	0.0	0.0	0.0	0.0
	Propylene (aromatics section)	0.0	0.1	0.1	0.1
	C4's (aromatics section)	0.0	1.0	1.0	1.0
	Benzene (aromatics section)	0.6	0.6	0.6	0.6
	P-xylene (aromatics section)	0.5	1.1	1.1	1.1
	O-xylene (aromatics section)	0.1	0.0	0.0	0.0
	Other products	2.1	1.7	3.6	1.8
	C7+ excess	0.0	0.2	0.2	0.2
	Wastewater	1.1	12.6	23.3	6.7

	Other waste	0.0	0.0	4.1	1.9
	Oxygen	0.4	21.9	8.5	0.3
	Other gases	0.5	7.3	3.0	1.7

Energy transport infrastructure will also be significantly affected. Changes range from under-utilisation of existing infrastructure to increases in flows by up to 1000 times. The significant changes in steam, condensate, cooling water, and electricity flows require upgrading or replacing pipelines, boilers, CHP units, and grid connections. These changes can also affect units outside the aromatic production system (SI Figures S23 and S24). For example, in the Port of Rotterdam, the cyclohexane plant currently shares LP steam with the aromatics plant. In the CO_2 and biomass-based cases, excess LP steam is produced. Therefore, less LP steam will be needed from the cyclohexane plant, resulting in an excess supply of LP steam for which a new user will need to be found or the heat will be wasted. This highlights the potential for unintended secondary ripple effects when ACS-based technologies are integrated into existing clusters.

Table 8: Utility needs or production at cluster level. A negative sign refers to heat produced, while a positive sign refers to cooling, heating or electricity needed. (Abbreviations: LLPS: Low-low pressure steam, LPS: Low pressure steam, MPS: Medium pressure steam, HPS: High pressure steam, HHPS: High-high pressure steam, HT: High temperature, CW: Cooling water)

Utility flow per unit of benzene (MJ/kg)		**Fossil-based Reference case**	**CO_2-based route**	**Biomass-based route**	**Plastic waste-based route**
In	LLPS	0	0	0	0
	LPS	4	0	0	51
	MPS	17	0	0	0
	HPS	7	0	0	0
	HHPS	2	0	0	0
	CW	31	289	477	148
	HT utility	0	0	0	103
	Electricity	1	1076	547	47
Out	LLPS	0	-3	-4	0
	LPS	0	-100	-100	0
	MPS	0	-3	-38	-49
	HPS	0	0	-132	-25
	HHPS	0	0	0	0

Another aspect to consider is the potential impact of defossilising benzene on the price of downstream products. In the reference cluster, the aromatics plant is interconnected through mass exchanges with four downstream value chains: ethylbenzene, aniline, cyclohexane and terephthalic acid. As a result, any changes in the MSP of benzene will cascade through these interconnected chains. Table 9 illustrates how price changes propagate through the various steps in each value chain. For instance, a 642% increase in the MSP of benzene leads to a 436% increase in the price of ethyl benzene, and a 299% increase in the price of propylene oxide/styrene monomer (PO/SM). Among the value chains considered in this study, the cyclohexane value chain is the most impacted, while the aniline value chain experiences the least impact. The lower impact of the aniline value chain can be explained by the fact that benzene is only one of the feedstocks needed for MDI production. Other chemicals, like nitric acid, formaldehyde and phosgene, are also used in the production of MDI, diluting the impact on the final product cost. Overall, the plastic-based MTA process has the smallest increase in benzene MSP and, consequently, the least impact on the aromatic value chains. Contrary, the CO_2-based MTA process triggers the highest price increases across the value chains due to its significantly higher benzene MSP.

Table 9: Change in MSP in the downstream value chain as a consequence of producing ACS-based aromatics (Abbreviations: PET: polyethylene terephthalate, PO: propylene oxide, SM: Styrene monomer, EB: Ethylbenzene, MDA-Methylenedianiline, MDI: Methylene diphenyl diisocyanate, PTA: pure terephthalic acid, WE: Water electrolyser, C2M: CO_2 to methanol, MTA: Methanol to aromatics, B2M: Biomass to methanol, P2M: Plastic to methanol)

Route	Value-chain	Price change
CO_2-based	Benzene → EB → PO/SM	+642% → +436% → +299%
	Benzene→ Aniline →MDA → MDI	+642%→+535%→ +384% → +171%
	Benzene → Cyclohexane	+642% → +521%
	P-xylene → PTA → PET	+642% → +472% →+ 318%
Biomass-based	Benzene → EB → PO/SM	+468% → +318% → +218%
	Benzene→ Aniline →MDA → MDI	+468% →+390% →+280% →+125%
	Benzene → Cyclohexane	+468% → +380%
	P-xylene → PTA → PET	+468% → +344% → +232%
Plastic waste-based	Benzene → EB → PO/SM	+145% → +98% →+67%
	Benzene→ Aniline →MDA → MDI	+145% → +121% → +87% → +39%
	Benzene → Cyclohexane	+145% → +118%
	P-xylene → PTA → PET	+145% → +107%→ +72%

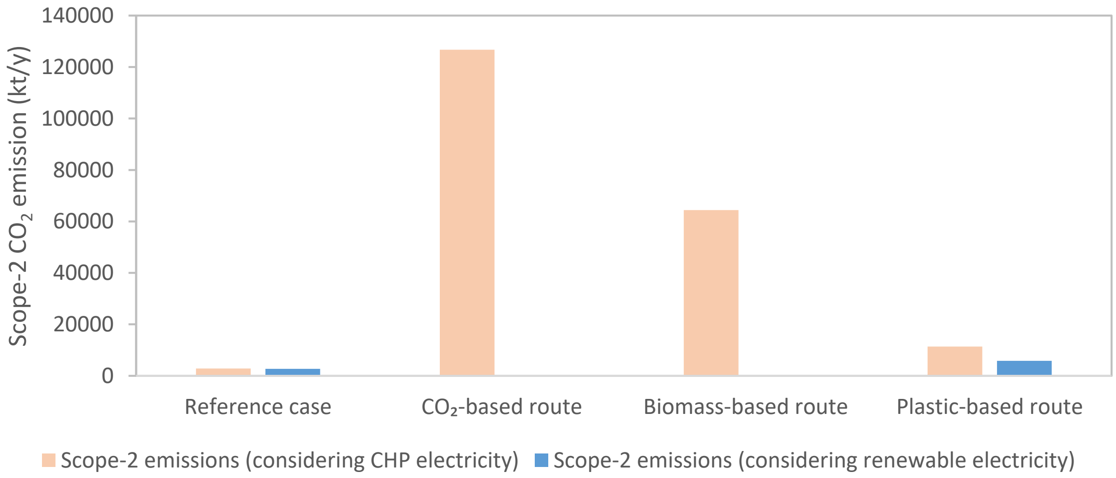

Figure 10: Scope-2 CO_2 emission of different ACS based routes for c.a1000 kt/y benzene production.

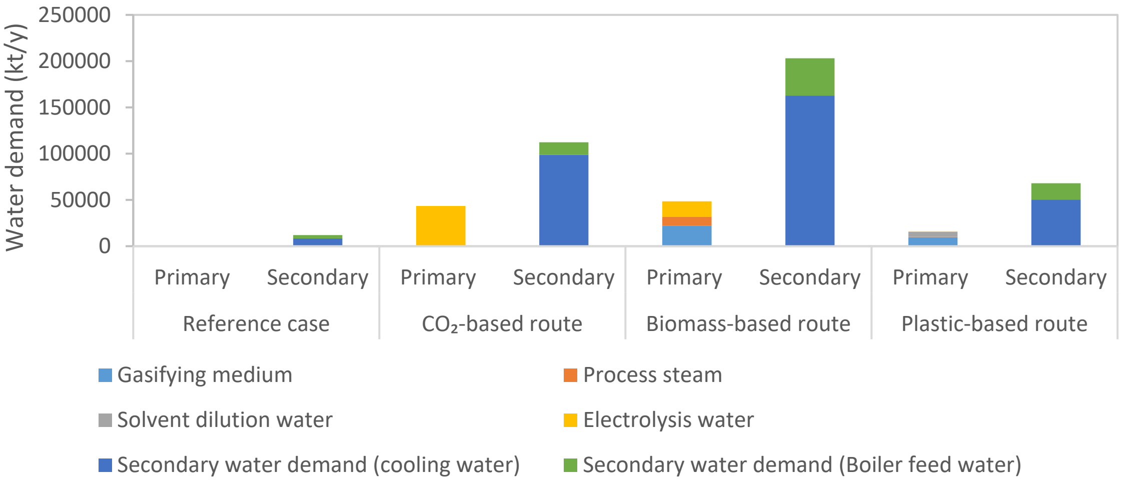

Figure 11: Primary and secondary water demand of ACS routes for about 1000 kt/y benzene production

The analysis of Scope-2 CO_2 emissions and secondary water demand (Figures 10 and 11) shows that relying on existing fossil-based utilities to supply energy significantly increases both CO_2 emissions and water demand at the cluster level. Note that the reference case appears to have lower CO_2 emissions, which is due to the selection of system boundaries in this study, where highly energy intensive upstream processes like crude distillation, naphtha hydrotreating, and naphtha catalytic reforming are not considered. Including Scope-3 emissions can change the comparative results, but this was outside the scope of this study.

For ACS-based processes, the main source of Scope-2 emissions is electricity consumption, particularly for hydrogen production in the CO_2 and biomass-based routes. Even when green hydrogen is assumed, these processes have higher Scope-2 emissions than the reference case (see SI Figure S26). This is due to the large operating pressure range (between 70 bar to 0 bar) in methanol-based process, which increases electricity demand (which is assumed to be taken from the existing grid). In the plastic waste-based production, Scope-2 emissions were due to external steam and process electricity needs. Figure 10 shows that plastic waste-based MTA routes appear with the lowest Scope-2 emissions. Note that if a defossilised energy grid would be available (Figure 10), scope 2 emissions would decrease by 49% for the plastic based process. While for the CO_2 and biomass based processes the emissions would decrease by 100%, as the scope-2 emissions from heat need is zero for these processes because they produce sufficient heat by offgas combustion and waste heat recovery. The findings highlight the importance of using renewable energy to provide electricity and heating utilities in ACS-based processes to mitigate their environmental impact.

Regarding secondary water demand, the largest contributor is make-up water for cooling systems. This is especially the case in gasification-based processes, operating at a high temperature range (~900 °C to -162 °C) (see SI Table S11). The high cooling demand highlights the need for improving heat integration strategies, such as low-temperature (<150 °C) heat recovery, to reduce cooling water requirements.

In general, the cluster-level comparison reveals several ripple effects triggered by defossilising aromatics production. These include excess propylene production, significant price impacts in downstream value chains (with cyclohexane being the most impacted), and high CO_2 emissions and water demand when existing fossil-based utilities and grid are used. However, this study has several limitations. Feedstock availability is not considered, utilities were not fully optimised, and technology learning curves were not considered. Further research should address these aspects.

3.3 Scenario Analysis

Figure 12 shows the result of the scenario analysis for benzene MSP. It shows that ACS-based processes are most fluctuating to electricity, solvent and feedstock prices for the boundary conditions assumed. For the CO_2-based MTA process, the most influential factors include electrolyser cost, electrolyser lifetime and electricity price. In the biomass-based MTA process, both hydrogen production and biomass gasification assumptions (electrolyser cost, electrolyser life, electricity price, feedstock price and solvent prices) significantly impact the MSP. For the plastic waste-based MTA process, the main driving factors are feedstock and solvent prices.

The CO_2-based process shows the highest MSP variation, ranging from 11 kEUR/t to 1.4 kEUR/t benzene (see SI Figure S27), due to the high fluctuation to electricity price and PEM cost for the boundary conditions assumed. The biomass-based process shows a moderate variation between 8.9 kEUR/t to 1.5 kEUR/t benzene (see SI Figure S28). The plastic waste-based process has the lowest MSP variation, from 3.2 kEUR/t to 1.2 kEUR/t benzene (see SI Figure S29), reflecting its lower dependence on hydrogen. Even under the most favourable scenario, all ACS-based technologies result in a benzene MSP higher than the reference case (1 kEUR/t). The scenario analysis (SI Figures S27 to S29) also highlights the importance of access to cheap electricity (~11 EUR/MWh), low PEM electrolyser cost (~580 EUR/kW), and high electrolyser lifetime (~25 years), for these technologies to be economically competitive.

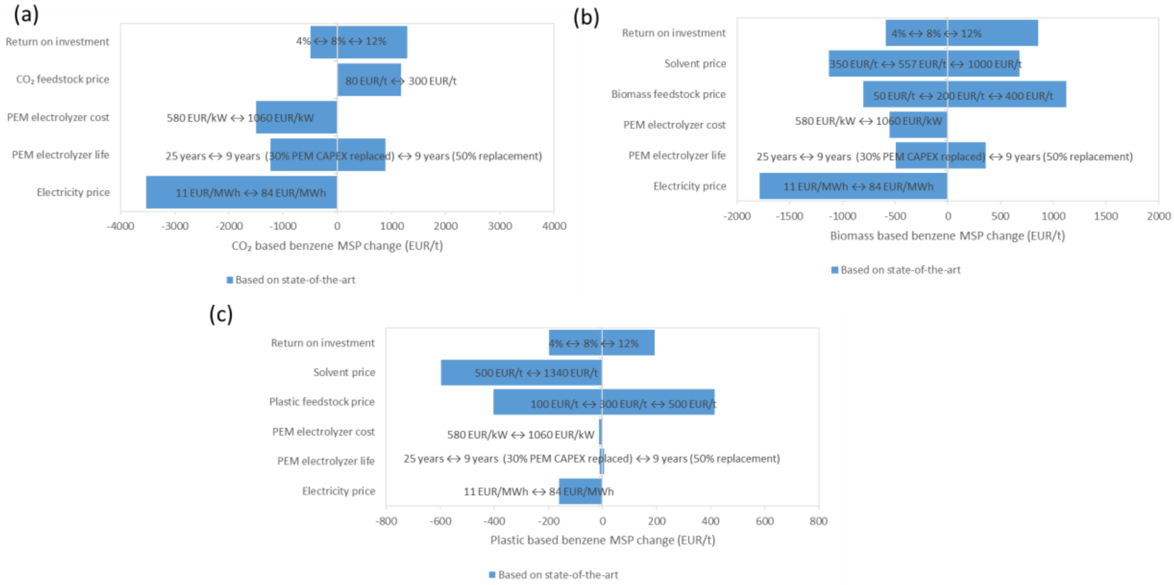

Figure 12: Scenario analysis in the MSP of (a) CO_2-based benzene, (b) biomass-based benzene, (c) plastic waste-based benzene

4. Conclusion

Transitioning away from fossil fuels in the production of high-volume petrochemicals like benzene is crucial for fully decoupling our society from fossil carbon sources. However, integrating alternative carbon source (ACS) technologies into highly interconnected petrochemical clusters can trigger unintended ripple effects across upstream supply chains, downstream units, waste treatment facilities, and utility systems. Using a case study based on an existing industrial cluster, the findings of this work reveal that for aromatics such as benzene, the transition is far from a plug-and-play solution. ACS processes differ significantly in product distributions, energy demands, production, and waste generation profiles. A major challenge for ACS-based benzene production technologies is their large electricity demand, particularly for hydrogen production. Cluster-level analysis highlights the added requirements for electricity, water, and waste treatment infrastructure, which may pose a significant challenge for industrial clusters.

Among the assessed ACS technologies, the plastic waste-based methanol to aromatics (MTA) process appears to result in the least disruptions to existing aromatics value chains. The results also show the impact of methanol production within the new chains, as it accounts for over 90% of electricity demand, CO_2 emissions (if existing utilities and grid are used), and water use. Unintended ripple effects, especially increased water consumption (primary and secondary) and high waste generation, could undermine the sustainability goals of defossilising aromatic production. Future research should focus on mitigating these challenges by exploring wastewater recycling, waste valorisation, low-temperature heat recovery. Ultimately, a clean energy mix, both for steam and electricity, remains a crucial requirement for integrating ACS-based processes into existing industrial clusters.

Even though plastic waste based technologies appear promising in Chapter 4 and Chapter 5, the ACS feedstock requirement is substantial. The impact of feedstock availability on the technology portfolio and performance of a cluster will be further studied in Chapter 6.

6. The impact of feedstock availability on defossilising the production of chemical building blocks

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This chapter is based on the manuscript Manalal J. T., Tan M., Pérez-Fortes M., Ramirez A. The impact of feedstock availability on defossilising the production of chemical building blocks. (submitted)

Chapter specific nomenclature & symbols

Nomenclature

ACS	Alternative carbon source	MDI	Methylene diphenyl diisocyanate
AD	Aromatics distillation	MO	Methanol to olefins
BM	Biomass to methanol	MPS	Medium pressure steam
BO	Biomass to olefins	MPW	Municipal plastic waste
CAPEX	Capital expenditure	MSP	Minimum selling price
CBB	Chemical building blocks	MTBE	Methyl tert-butyl ether
CHP	Combined heat and power	NSC	Naphtha steam cracking
CM	Carbon dioxide to methanol	OPEX	Operational expenditure
CO	Carbon dioxide to ethylene	PET	Polyethylene terephthalate
CW	Cooling water	PGME	Propylene glycol methyl ether
DME	Dimethyl ether	PLTP	Plastic waste low-temperature pyrolysis
EB	Ethylbenzene	PM	Plastic waste to methanol
EDC	Ethylene dichloride	PO	Propylene oxide
EO	Ethylene oxide	PoR	Port of Rotterdam
HHPS	High-high pressure steam	PTA	Purified terephthalic acid
HPS	High pressure steam	PVC	Polyvinyl chloride
HT	High temperature	SMR	Steam methane reforming
IPA	Isopropyl alcohol	SPW	Sorted plastic waste
KPI	Key performance indicator	TBA	Tert-butyl alcohol
LLPS	Low-low pressure steam	VGO	Vacuum gas oil
LPS	Low pressure steam	WE-L	Water electrolysis- Large
MA	Methanol to aromatics	WE-S	Water electrolysis- Small

Symbols

GW	Gigawatt	Mt	Million tonnes
kt	Kilotonne	PJ	Petajoule
MJ/kg	Megajoule per kilogram	TWh	Terawatt hour

Abstract

Chemical building blocks such as methanol, ethylene, propylene, benzene and p-xylene are produced from fossil-based feedstocks like natural gas, naphtha, reformates and pyrolysis gasoline. Alternative carbon sources (ACS) such as CO_2, biomass and plastic waste can be used in technologies like hydrogenation, gasification, dehydration, pyrolysis and cracking to defossilise conventional chemical building blocks (CBB). While existing literature estimates the quantities of ACS to replace fossil fuel in specific processes, hubs or areas, and explores theoretical upper limits, the impact of feedstock availability and the resulting consequences of implementing ACS-based processes on the performance of existing clusters have not been explored. This work aims to evaluate eight ACS-based processes for CBB production to meet the current production in an existing cluster in the Netherlands. The results highlight that if feedstocks were unlimitedly available, plastic waste-based pyrolysis, methanol-to-olefin, and methanol-to-aromatics routes appear to be the most promising technologies. However, when considering feedstock constraints, a combination of ACS and fossil-based technologies is required to meet product demand, and the level of defossilisation significantly decreases. This research underscores the critical need to balance technological choices and realistic assessments of ACS feedstock availability to ensure a sustainable and economically viable transition for the chemical industry.

1. Introduction

Day-to-day essentials like packaging, cosmetics, medicines, fertilisers, detergents, paints and fuels are made from fossil-based raw materials such as crude oil or natural gas.[2] In order to reach ambitious CO_2 emission reduction targets needed to mitigate climate change, replacing the use of fossil-based feedstocks with sustainable carbon feedstocks (i.e. defossilisation) will be vital.[2]

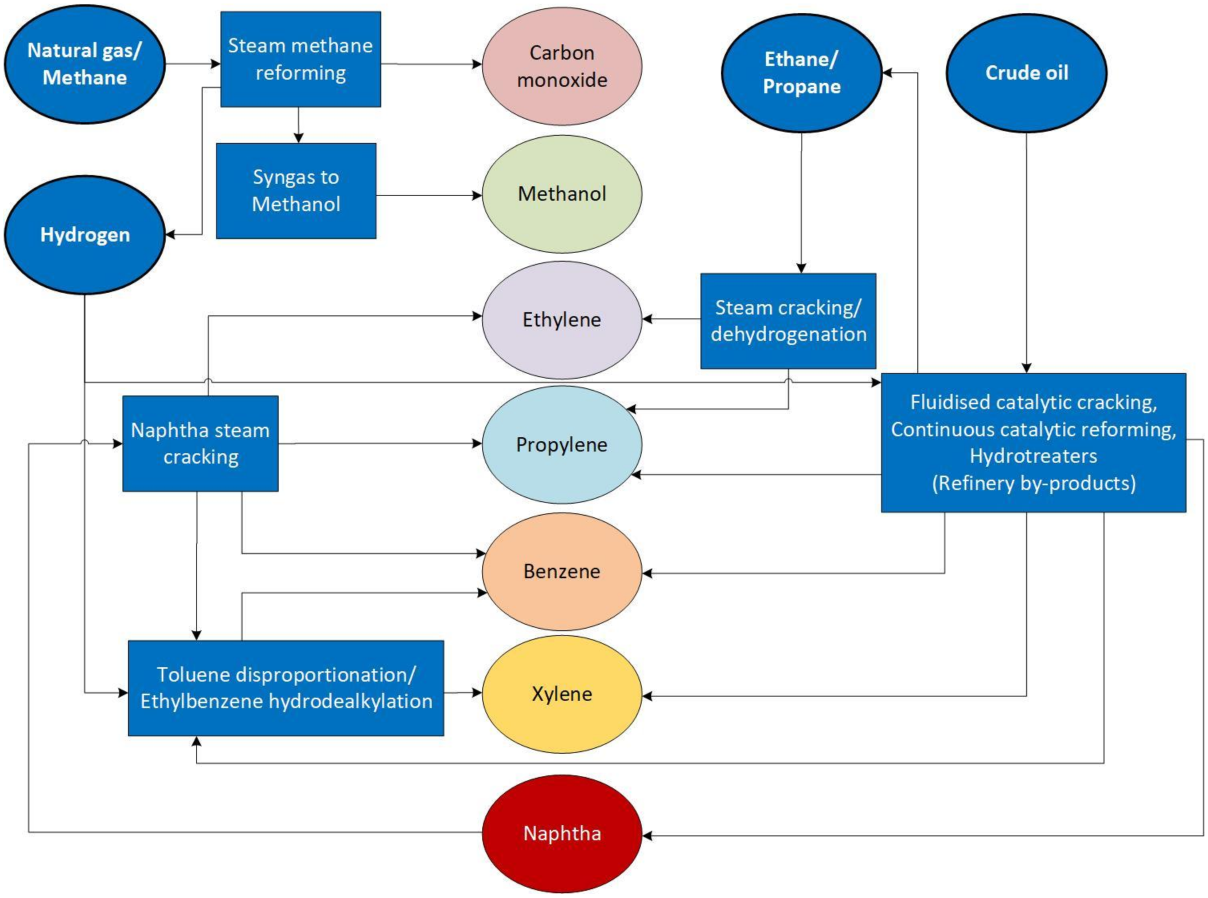

Figure 1. Overview of fossil-based feedstocks and technologies typically used for the production of chemical building blocks.

In today's petrochemical industry, fossil-based raw materials such as crude oil or natural gas are first broken down into chemical building blocks (CBB) such as carbon monoxide, methanol, ethylene, propylene, benzene and xylene before further processing (see Figure 1). These CBB are the backbone of the chemical sector. They can be defossilised by using alternative carbon sources (ACS) such as CO_2, biomass and plastic waste as feedstocks. Despite the increasing interest, several studies[3,53–56,58,136] have raised concerns about current and future ACS availability. In a study by the Royal Society[3] aiming to identify the challenges of defossilising the chemical industry, it was estimated that globally, 7000 Mt of sustainable biomass (wet) will be needed for a net-zero emission from the chemical industry[3]; but only 4300 Mt biomass (wet) is available globally (as of 2022).[3]

Regarding plastic waste feedstock availability, low recycling rates and high energy intensity of waste-to-chemical processes were the main challenges identified in the study.[3] Currently, approximately 300 to 400 Mt of plastic are produced globally, and only about 9% are recycled, raising questions about the feedstock availability for waste-to-chemical processes. For CO_2 feedstock, the same study estimated a CO_2 demand of 2800 Mt to 4700 Mt, which is less than 1% of the annual anthropogenic CO_2 emissions in 2022 (~59000 Mt CO_2).[3] However, as indicated by Lopez et al[55], the main challenge for CO_2-based chemical production is the large energy requirement for direct electrochemical reduction or hydrogen production. The authors estimated that around 30000 TWh to 40000 TWh of electricity will be required to satisfy the CO_2-based global chemical sector. Currently, about 30000 TWh of electricity is generated globally (as of 2023)[57], which means that an additional electricity equivalent to current global production will be required for a CO_2-based chemistry transition. Zanon-Zotin et al[54]., estimated that with limitations on alternative feedstocks and renewable electricity availability, only about 28% of the global primary chemical sector could be defossilised. [54]

A similar picture has been reported at the European level. For instance, Bazzanella et al[42] estimated that by 2050, Europe will need around 4900 TWh of green electricity (140% of the projected available supply), 300 Mt of CO_2 feedstock (corresponding to c.a. 80% of large source emissions) and 250 Mt of dry biomass (30% of the available sustainable and non-food based biomass in Europe).[42] For plastic waste feedstock, most studies[3,42,137] do not provide an estimate of the required feedstock, however, they report that Europe produces around 49 Mt of plastics, of which only about 10% (~5 Mt) is recycled, and the rest is lost as export, stockpile, misclassified waste, unsorted waste, landfill, and for energy recovery.[137]

In the Netherlands, Lucas et al.,[53] studied the potential of ACS for the transition of the Port of Rotterdam (PoR) and estimated that biomass, bio-oils, plastic waste and pyrolysis oil could only replace up to 40% of the total carbon feedstock demand in the PoR industrial cluster. The study[53] did not make explicit how the limit was calculated but they indicated that the low feedstock replacement was due to the lower energy densities and conversion efficiencies of ACS and technologies compared to fossil-based counterparts.[53]

Even though such studies[3,42,53,54,58,59] provide valuable insights into the amount of ACS required or the limit up to which the chemical sector can be defossilised, these are top-down studies which do not take into account existing processes, conditions and geographical limitations of today's petrochemical clusters and usually assume green-field conditions. For instance, in the study by Lucas et al[53] , the authors discussed the potential ACS-based pathways for defossilisation, but did not address how feedstock availability affects the technology deployment and performance of the cluster. As identified by Samadi et al[52], defossilising a highly integrated petrochemical cluster can impacts its performance because of changes in energy, product portfolios, investments and ACS feedstock availability.[52] To date, top-down studies[52,53,59] in the literature do not quantify these impacts. This chapter aims to address this knowledge gap by assessing how feedstock and energy limitations for biomass, plastic waste, and electricity could potentially change their technology deployment for defossilising CBB production and consequently the performance of existing petrochemical clusters. The article's main contribution is its bottom-up analysis of how feedstock limitations and existing conditions affect technology choices, investment requirements, water use, energy consumption, and by-product generation in a highly interconnected industrial cluster.

2. Methodology

A superstructure-based multi-objective optimisation model was used to explore optimal technology portfolios under different feedstock availability cases for defossilising CBB production in a petrochemical cluster. The selected CBBs were methanol, ethylene, propylene, benzene and p-xylene. Fossil feedstocks considered in the reference case were: carbon monoxide, methanol from natural gas, and propylene, C4's, naphtha, pygas, reformate from oil; while the defossilisation cases considered CO_2, biomass and plastic waste as ACS-based feedstocks. Both the fossil and ACS-based technologies were modelled in Aspen Plus v12 with capacities and product purities mimicking CBB production in the Port of Rotterdam (PoR), the Netherlands. The energy, mass and investment data from the Aspen Plus models were used in the optimisation model for the technology portfolio analysis.

2.1 Optimisation model

The optimisation model used has been reported in Tan et al.[99,138] (see Appendix D) and includes a multi-layered graph representation of energy, mass and equipment (capital expenditure - CAPEX) data.[138] The model is described in detail when discussing the reference case. For this work, two objective functions (Eq. 1) were defined to find the optimal technology portfolio that (a) minimises the amount of fossil carbon used for CBB production and (b) maximises the use of existing assets in the cluster, as companies are likely to try to use assets that are already in place.

The amount of fossil carbon used in the cluster ($Carbon_{Fossil}^{Import}$) was calculated as the sum of carbon in fossil-based feedstocks FM_{FC} (see Eq. 2), i.e. in carbon monoxide, methanol, propylene, C4's, naphtha, pygas, reformate and natural gas. To maximise use of existing assets and minimise new investments, Eq. 3 was used, where a CAPEX penalty was defined as the sum of investments required for the new ACS technologies plus the loss of existing CAPEX as a consequence of dismantling fossil-based processes.

$$min\left(Carbon_{Fossil}^{Import}, CAPEX\ penalty\right) \tag{1}$$

$$Carbon_{Fossil}^{Import} = \sum_{f\ \in FM_{FC}} Feed_f^{Mass} * m_f^{Carbon} \tag{2}$$

$$CAPEX\ penalty = \left(\sum_{p \in PP_{Fossil}} \left(1 - p_p^I\right) * CAPEX_p + \sum_{p \in PP_{ACS}} p_p^I * CAPEX_p \right) \tag{3}$$

Where, *f* is the carbon feedstock, FM_{FC} is the set of fossil-based carbon feedstock; $Feed_f^{Mass}$ is the mass flow of the inlet carbon feedstock *f*; m_f^{Carbon} is the mass fraction of carbon in the fossil-based feedstock *f*; *p* is the CBB production process, which can use either fossil or alternative carbon sources; PP_{Fossil} is the set of fossil-based processes; PP_{ACS} is the set of ACS-based processes; p_p^I is the integer value representing the number of plants per process *p*; and $CAPEX_p$ is the total capital expenditure required for process *p*.

In the model two constraints were applied. First, the same amount of final products had to be produced as in the reference case (fossil feedstock based case) (see Eq. 4), within an upper demand margin of 20% (1.2 in Eq. 4) and 10% of operational margin (denoted as operational flexibility, K_p^{Flex}- see Eq. 5). Second, the maximum amount of feedstock available could not be surpassed (Eq. 6); the limitations are given in the feedstock availability section, below.

$$\left(1 - K_d^{Tol}\right) \le \frac{Mass_{d,cc}^{Out}}{X_{d,cc}^{Demand}} \le 1.2 \quad \forall d \in D, \forall cc \in CC \tag{4}$$

$$\left(1 - \frac{K_p^{Flex}}{10^4}\right) * p_p^I * K_{p,cc}^{Cap} \le Mass_{p,cc}^{Out} \le p_p^I * K_{p,cc}^{Cap} \quad \forall\ p \in PP_{ACS} \cap PP_{Fossil}, \forall\ cc \in CC \tag{5}$$

$$Feed_f^{Mass} \leq Limit_{ACS} \forall f \in FM_{ACS} \tag{6}$$

Where, K_d^{Tol} is the tolerance parameter of the lower demand constraint; $Mass_{d,CC}^{Out}$ is the mass flow of product of the demand node *d*; $X_{d,cc}^{Demand}$ is the reference case production rate of each CBB, *CC* is the set of chemical building blocks, and *cc* is the chemical building block; *D* is the set of demands of each chemical building block and *d* is the demand of each chemical building block; K_p^{Flex} is the operational flexibility parameter of process *p*, $K_{p,cc}^{Cap}$ is the nominal production capacity of component *cc* of process *p*; *f* is the carbon feedstock, $FM_{ACS}$is the set of ACS-based carbon feedstock, $Feed_f^{Mass}$is the mass flow of the inlet carbon feedstock, and $Limit_{ACS}$ is the alternative carbon feedstock limit.

The optimisation model was run for three cases: the reference case (Case 1), a case with unlimited availability of ACS feedstock (Case 2), and a case with limited ACS feedstock availability (Case 3). The reference case was run to obtain the CAPEX, inlet fossil carbon, product flows and energy needs of the fossil-based cluster. For Case 2, only Eq. 4 and Eq.5 were used as constraints, while for Case 3, Eq. 4, Eq. 5 and Eq. 6 were used as constraints. The optimisation model was solved using the augmented ε-constraint method, which generated a set of technology portfolio solutions as a Pareto front for each case.[138] From the Pareto front, using Eq. 7, the solutions that achieved 55%, 75% and 95% defossilisation of CBB with a deviation of ± 1% were selected and discussed in this work.

$$Defossilisation\,\% = \frac{Carbon(ref)_{Fossil}^{Import} - Carbon(i)_{Fossil}^{Import}}{Carbon(ref)_{Fossil}^{Import}} * 100 \tag{7}$$

Where, $Carbon(ref)_{Fossil}^{Import}$ is the fossil-based carbon entering into the cluster for the reference case and $Carbon(i)_{Fossil}^{Import}$ is the fossil-based carbon entering into the cluster when using the ACS-based technologies in Cases 2 and 3.

The technology portfolios were compared using the following key performance indicators (KPIs): percentage of defossilisation (Eq. 7), CAPEX penalty (Eq. 3), amount of feedstocks usage ($Feed_f^{Mass}\ \forall f \in FM_{FC}\ \ and\ Feed_f^{Mass}\ \forall f \in FM_{ACS}$), mass flows of byproducts ($Mass_{d,CC}^{Out}$), energy needs and average selling price of each CBB. The energy need was calculated as the net utility flow of the CBB production processes, as given in Eq. 8.

$$Energy\ need\ = \sum_{p \in PP_{ACS} \cap PP_{Fossil}} Mass_{p,cc}^{In} * X_{p,cu}^{Demand} - Mass_{p,cc}^{In} * X_{p,cu}^{Supply}\ \forall cu \in CU \tag{8}$$

Where, *CU* is the set of utilities considered, $Mass_{p,cc}^{In}$ is the component stream (i.e., for example ethylene in the case of naphtha cracker) on which the process streams are linearised, *cu* is the utility type and $X_{p,cu}^{Supply}$ is the specific energy production with respect to the limiting component $Mass_{p,cc}^{In}$ for the process *p* and utility *cu*, $X_{p,cu}^{Demand}$ is the specific energy need with respect to the limiting component $Mass_{p,cc}^{In}$ for the process *p* and utility *cu*.

The average selling price of each CBB was calculated from its minimum selling price (MSP) using Eq. 9 and Eq. 10, and assuming a payback period of 12 years.

$$\sum_{cc\in CC} Mass_{p,cc}^{Out} * MSP_{p,cc} = \frac{CAPEX}{Payback\ period} + OPEX\ \forall\, p\ \in PP_{ACS} \cap\ PP_{Fossil} \tag{9}$$

$$MSP_{cc} = \frac{\sum_{p\in PP_{ACS}\cap PP_{Fossil}} Mass_{p,cc}^{Out} * MSP_{p,cc}}{\sum_{p\in PP_{ACS}\cap PP_{Fossil}} Mass_{p,cc}^{Out}}\ \forall cc \in CC \tag{10}$$

2.2 Fossil-based cluster (reference case)

This study takes as a point of departure the petrochemical cluster in the PoR, the Netherlands. The PoR is part of the largest chemical cluster zone in Europe (the Antwerp-Rotterdam-Rhein-Ruhr economic zone), which is responsible for 30% to 40% of the chemical production in Europe.[139] The reference cluster in this study includes 57 chemical processes and their utility islands, which were modelled in Aspen Plus v12.[99] The modelling assumptions, bibliographic sources, material, energy and cost data for the reference case petrochemical cluster are reported in the supplementary information. The reference cluster is described in detail in Tan et al's work. [99,138]

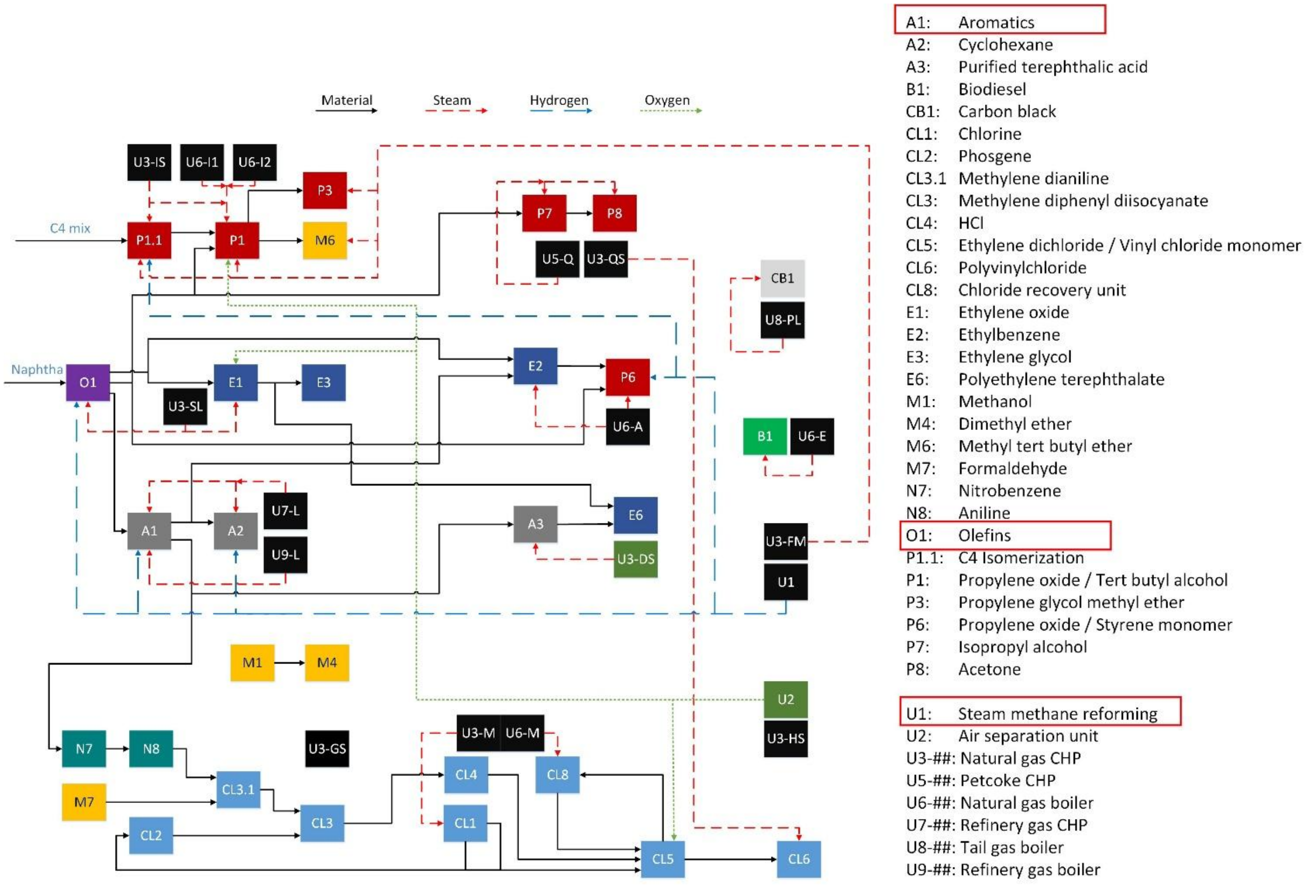

Figure 2. Simplified diagram of the petrochemical cluster used as reference case. The diagram presents the main mass and energy flows. The red boxes show the CBB production considered in this study. (Abbreviations: CHP- Combined heat and power plant).

The main mass flows in the reference case are shown in Figure 2 (adapted from Tan et al[99]). It includes the naphtha steam cracker (NSC) for the production of ethylene, propylene, benzene (O1 in Figure 2); aromatics distillation (AD) for the production of benzene, p-xylene (A1 in Figure 2), and steam methane reformer (SMR) for the production of hydrogen (U1 in Figure 2). All processes were designed to produce products with 99.5 wt% purity. As the design basis, we considered the technical specifications shown in

Table 1. 2018 was used as the base year, plant life was assumed to be 25 years, located in the Netherlands (Rotterdam). In the reference case, the carbon feedstocks imported for CBB production were carbon monoxide, methanol, propylene, C4's, naphtha, pygas, reformate and natural gas. Even though propylene and C4s were produced in the cluster in the NSC process, approximately 20% of the total propylene demand and 75% of the total C4s demand in the cluster are met by imports. The reference case included the following utilities: low-low pressure steam (LLPS), low pressure steam (LPS), medium pressure steam (MPS), high pressure steam (HPS), high-high pressure steam (HHPS), cooling water (CW), refrigerants, high temperature (HT) utility and electricity; as detailed in Table 3 of Chapter 4.

Table 1. Reference case technologies for chemical building block production (detailed data of the process models are provided in the SI).

Chemical	**Technology**	**Design basis**			
		Capacity	**Feedstock**	**Reactor**	**Downstream processing**
Hydrogen	Steam methane reformer (SMR)	118 kt/y hydrogen	Natural gas (71% methane)	Steam reforming at 850 °C, 17 bar	Pressure swing adsorption
Methanol	Steam methane reformer (SMR)	90 kt/y methanol	Natural gas (71% methane)	Steam reforming at 900 °C, 20 bar; Syngas to methanol at 255 °C, 70 bar	High pressure distillation
Olefins	Naphtha steam cracker (NSC)	878 kt/y ethylene and 497 kt/y propylene	Full range naphtha	Steam cracking at 850 °C, 5 bar	Cryogenic distillation
Aromatics	Aromatics distillation (AD)	892 kt/y benzene and 754 kt/y p-xylene	Pygas and reformate	Toluene disproportionation at 400 °C, 30 bar; Xylene isomerisation at 400 °C, 14 bar	Extractive distillation

2.3 Ex-ante ACS technologies

Eight ACS-based pathways (see Table 2) for the production of methanol, ethylene, propylene, benzene and p-xylene were analysed in this study. Potential ACS technologies were modelled in Aspen Plus v12, as described in Chapter 2 and previous work[79,134]. Two green hydrogen plants, water electrolysis-small (WE-S) and water electrolysis-large (WE-L), with hydrogen production capacities of 17 kt/y and 110 kt/y, respectively, were used to provide the required hydrogen for the selected ACS-based processes. The green hydrogen-based plants were mainly required for the hydrogenation process steps in the CO_2 or biomass-based processes, as these feedstocks have a zero (for CO_2) or low hydrogen to carbon mole ratio (H:C of 1.7) compared to the fossil-based feedstocks (H:C of 4 and 2.2 for methane and naphtha, respectively). The capex for hydrogen production is included in the optimisation model as required by the defossilised cluster. The descriptions, block flow diagrams, mass balances, energy balances and CAPEX of the processes are provided in the SI Section 2, Figure S1 to Figure S12 and Table S2 to Table S14. The detailed dataset of each process model can be found in the project repository, indicated in the SI.

Table 2. Selected ACS-based technologies for chemical building block production (detailed data of the process models are provided in the SI).

Chemical	**Technology**	**Design basis**			
		Capacity	**Feedstock**	**Reactor**	**Downstream processing**
Hydrogen	Water electrolysis (WE)	17 kt/y hydrogen (WE-S); 110 kt/y hydrogen (WE-L)	Water	Proton exchange membrane electrolyser at 80 °C, 1.02 bar	Flash drum, molecular sieve
Methanol	CO_2 hydrogenation to methanol (CM)	406 kt/y methanol	Food grade CO_2	Hydrogenation reactor at 255°C, 70 bar	High-pressure distillation
	Biomass steam gasification to syngas + syngas to methanol (BM)	414 kt/y methanol	Wood pellet	Steam gasifier at 830 °C, 2 bar; Hydrogenation reactor at 255°C, 70 bar	Solid-gas separation, tar removal, acid gas cleaning, cryogenic distillation, high-pressure distillation
	Plastic waste steam gasification to syngas + syngas to methanol (PM)	408 kt/y methanol	Municipal plastic waste (Netherlands)	Steam gasifier at 900 °C, 1.02 bar; Hydrogenation reactor at 255 °C, 70 bar	Solid-gas separation, tar removal, high-pressure distillation
Olefins	Direct electrochemical reduction of CO_2-H_2O to ethylene (CO)	329 kt/y ethylene	Food grade CO_2	Steam cracking at 80 °C, 1.1 bar	Molecular sieve, cryogenic distillation
	Biomass steam gasification to syngas + syngas to Fischer-Tropsch and methanol + methanol to olefin (BO)	301 kt/y ethylene and 298 kt/y propylene	Wood pellet	Steam gasifier at 830 °C, 2 bar; Fischer-Tropsch at 340 °C, 30 bar; Hydrogenation reactor at 255 °C, 70 bar; Methanol to olefin at 450 °C, 30 bar	Solid-gas separation, tar removal, acid gas cleaning, cryogenic distillation
	Plastic waste low temperature pyrolysis (PLTP) + Naphtha steam cracking (NSC)	303 kt/y ethylene and 172 kt/y propylene	Sorted plastic waste (Deutsche Kunststoff Recycling 329 and Deutsche Kunststoff Recycling 324)	Pyrolysis reactor at 420 °C, 1.02 bar; Steam cracking at 850 °C, 5 bar	Vacuum distillation, cryogenic distillation

	Methanol-to-olefins (MO)	314 kt/y ethylene and 398 kt/y propylene	Methanol	Methanol-to-olefin at 450 °C, 30 bar	Solid-gas separation, cryogenic distillation
Aromatics	Methanol-to-aromatics (MA)	535 kt/y benzene and 972 kt/y p-xylene	Methanol	Methanol-to-aromatics at 450°C, 60 bar; Toluene disproportionation at 400 °C, 30 bar; Xylene isomerisation at 400 °C, 14 bar	Solid-gas separation, cryogenic distillation, extractive distillation

Note: The ACS-based process are modelled to produce methanol, ethylene and benzene in the range of 400-415 kt/y, 300-330 kt/y and 530-540kt/y respectively. The production range is selected to meet 1/3rd demand of olefins and aromatics in the reference case petrochemical cluster.

2.4 Feedstock availability

ACS feedstock limitations were assumed based on the reported availability of these feedstocks in the Netherlands. Given the importance of the transition, when possible, the upper limit was selected. Although CO_2 availability is not limited as it could be obtained from the atmosphere via direct air capture, the amount of renewable energy needed to use this feedstock is limited. Using a renewable electricity generation limit of 200 PJ/y[60], which is in line with the expected electricity use by the Dutch industry in a 2030-2050 scenario[140], a CO_2 feedstock limit of 3 Mt/y was estimated. A biomass supply limit of 8 Mt/y in the Netherlands was assumed based on Rabou et al.,[62] (see SI Table S15 for a detailed breakdown of biomass types and quantities). The estimated plastic waste collection in the Netherlands is about 1.9 Mt/y[141] while the total production of plastics is estimated to be 6.2 Mt/y[61]. This large difference between production and collection is because about 3.8 Mt/y of plastic is exported outside the Netherlands, and only about 2.3 Mt/y is used locally.[61] Based on this, a municipal plastic waste (MPW) limit of 2 Mt/y was assumed. Also, considering the global plastic waste trade of 12 to 6 Mt/y[142] and plastic waste generation of 30 Mt/y[143] in the EU 28+2 (see SI Table S16), an additional plastic waste source, sorted plastic waste (SPW) with a limit of 5 Mt/y, was assumed in the study.

3. Results and discussion

3.1 Case 1 (Reference case)

In the reference case, about 7.2 Mt/y of fossil carbon are required in the cluster as feedstock to produce approximately 3.4 Mt/y of CBB for the different value chains considered in this study. As seen in Figure 3, the import of naphtha, pygas and reformate for olefins and aromatics production accounts for 86% of the inlet fossil carbon flow in the cluster. In the reference case, 100% of the methanol demand (293 kt/y) is met by imports. Natural gas is used for the production of grey hydrogen and DME. The highest amounts of waste and by-products come as heavy hydrocarbons (2969 kt/y from the aromatics plant) and as off-gases (893 kt/y from the steam methane reformer and 641 kt/y from the olefins plant). Around 114 kt/y hydrogen, 1.3 Mt/y olefins and 2 Mt/y aromatics are produced in the reference cluster. As shown in Table 3, aromatics constitute the highest CBB production, accounting for 60% of the CBB mass flow in the cluster.

In terms of water demand, 1.3 Mt/y is used by the naphtha steam cracker and 0.7 Mt/y is used by the steam methane reformer. The aromatics plant does not need external water.

In the reference case, the considered CAPEX includes a naphtha steam cracker (1.1 billion EUR), an aromatics distillation unit (0.7 billion EUR), and a steam methane reformer (0.3 billion EUR). Thus, even though aromatics account for the highest production, the most expensive contribution comes from the olefin production plant. The average selling prices of the methanol, olefins and aromatics calculated from the model are around 650 EUR/t, 1000 EUR/t and 880-1100 EUR/t, respectively.

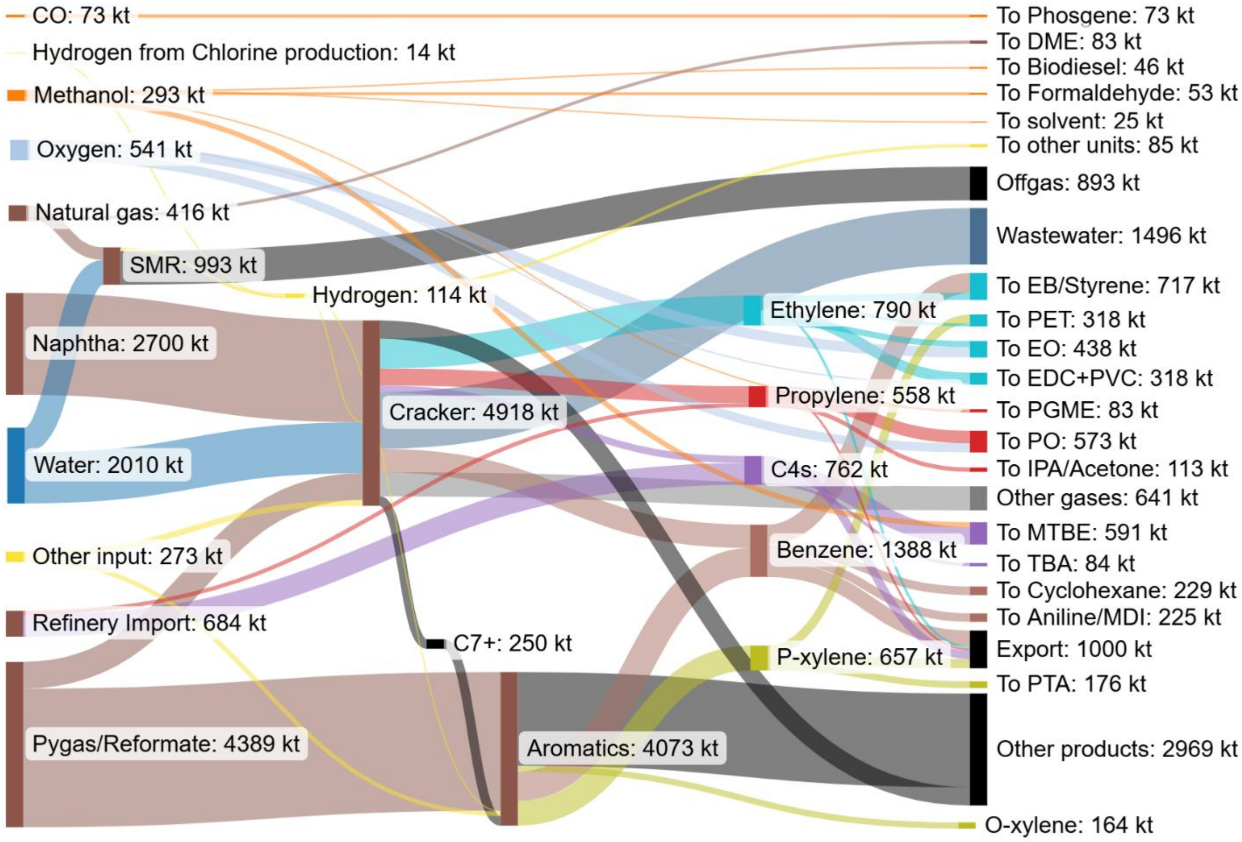

Figure 3. Sankey diagram of mass flows per year for Case 1 (Abbreviations: EO- Ethylene oxide, EDC- Ethylene dichloride, DME- Dimethyl ether, PVC- Polyvinyl chloride, PET- Polyethylene terephthalate, EB- Ethylbenzene, PO- Propylene oxide, PGME- propylene glycol methyl ether, IPA- Iso-propyl alcohol, MTBE- Methyl tert-butyl ether, TBA- Tert-butyl alcohol, MDI- Methylene diphenyl diisocyanate, PTA- Purified terephthalic acid, SMR- Steam methane reformer)

In terms of energy, out of the 7 PJ/y electricity needed for the CBB production plants in the cluster, 6.6 PJ/y is used by the naphtha steam cracker, and about 85% of it is for the cryogenic-based high-pressure product distillation section. All the CBB production routes are endothermic due to the cracking and reforming reactions involved. However, off-gases are combusted to produce 15 PJ of steam. This reduces the steam needs from 31 PJ to around 16 PJ in the cluster.

Table 3. Portfolio of technologies, CAPEX, mass flows, energy flows and average minimum selling price of CBB in Case 1 (reference case). The negative sign (-) refers to heat production and positive sign (+) refers to cooling, heating or electricity needs in the energy needed or produced column. (Abbreviations: SMR: steam methane reformer, NSC: naphtha steam cracker, AD: aromatics distillation, SPW: sorted plastic waste, MPW: municipal plastic waste, CBB: chemical building block, LLPS: Low-low pressure steam, LPS: Low pressure steam, MPS: Medium pressure steam, HPS: High pressure steam, HHPS: High-high pressure steam, HT: High temperature, CW: cooling water)

Case	**Technologies (number of units)**	**CAPEX (Billion EUR)**	**Fossil feedstocks (kt/y)**	**Alternative feedstocks (kt/y)**	**Energy needed or produced (PJ/y)**	**CBB production (kt/y)**	**Average minimum selling price (EUR/t)**
Reference case	Hydrogen: 1 SMR Methanol: Imported fossil methanol Naphtha: Imported fossil naphtha Olefin: 1 NSC Aromatics: 1 AD	2	CO: 73 Methanol: 293 Propylene: 110 C4: 574 Naphtha: 2700 Pygas: 2334 Reformate: 2055 Natural gas: 416	CO_2: 0 Biomass: 0 SPW:0 MPW: 0	LLPS: 0.2 LPS: 11 MPS: 10 HPS: -0.3 HHPS: -1.5 HT: 4.2 Electricity: 7 CW: 48	Ethylene: 790 Propylene: 558 Benzene: 1388 P-xylene: 657	Ethylene: 1075 Propylene: 1000 Benzene: 884 P-xylene: 1105

3.2 Case 2 (Defossilisation without limitations on feedstock availability)

The multi-objective optimisation resulted in the Pareto fronts shown in Figure C1 of Appendix C. As shown in Table 4, the deployment of the ACS-based processes results in up to 95% defossilisation in Case 2, by reducing the total amount of fossil carbon from 7.2 Mt to 0.5 Mt, using about 19.5 Mt of plastic waste. Regardless of the defossilisation target, the results show that technologies that use plastic waste as feedstock are selected in all cases (reaching up the 95% defossilisation) while the CO_2 or biomass-based technologies are not part of the technology portfolio.

Plastic waste-based technologies show the lowest CAPEX penalty per tonne of product, as they require the least amount of hydrogen. For instance, to produce 400 kt of methanol, plastic waste-based methanol process requires around 403 MEUR of CAPEX, while the biomass and CO_2-based methanol processes need 2050 million EUR and 2903 million EUR, respectively. This high CAPEX for CO_2 and biomass-based technologies is mostly due to the hydrogen requirements; hydrogen production through water electrolysis contributes about 46% and 86% of the inside battery limit related CAPEX for biomass and CO_2-based processes, respectively. As seen in Figure 4, the major share of the CAPEX penalty due to defossilisation in Case 2 is accounted for by the plastic waste feedstock to methanol (i.e., plastic waste steam gasification followed by syngas to methanol) and naphtha (i.e., plastic waste pyrolysis) production processes, due to their high cost of implementation. The CAPEX loss from the removal of existing fossil-based processes only accounts for 6% of the CAPEX penalty.

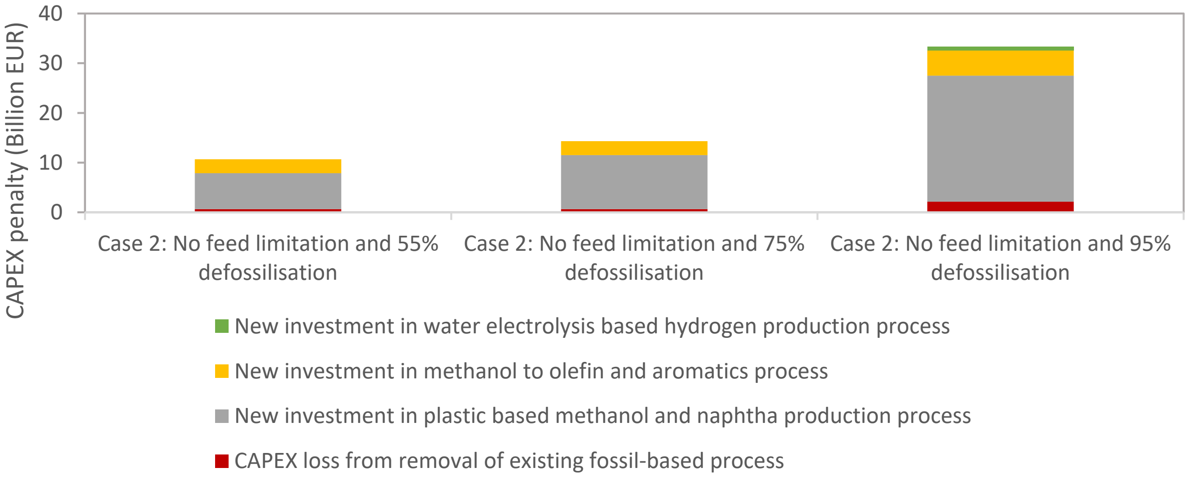

Figure 4. Breakdown of CAPEX penalty in Case 2 for 55%, 75% and 95% defossilisation targets.

In the 55% defossilisation scenario, the amount of fossil carbon used in the cluster is reduced by fully replacing the fossil-based production of aromatics (benzene, p-xylene) with an ACS-based methanol-to-aromatics process and by partially defossilising the olefin production using synthetic naphtha produced through the plastic waste-based pyrolysis route. In this scenario, 78% of the naphtha is produced from the plastic waste-based pyrolysis process, which requires around 10 Mt of sorted plastic waste. For comparison, the global plastic waste trade is about 8 to 14 Mt.[142] In addition to the sorted plastic waste, about 4 Mt of municipal plastic waste is required in this scenario for the production of methanol. Thus, substantial quantities of plastic waste (14 Mt), equivalent to that available in the global trade, would be required in this scenario.

The 55% and 75% defossilisation scenarios have the same technology portfolio (see in SI Figures S18 and S20 their technology portfolio), while the main difference is in the amount of methanol imported vs produced in the cluster (see SI Figure S18 to Figure S21). In the 55% defossilisation scenario, about 3.5 Mt of fossil-based methanol is imported, while in the 75% defossilisation scenario, all the required methanol is produced inside the cluster. This additional methanol production inside the cluster (i.e., 3.5 Mt methanol) leads to an extra demand of 2.8 Mt of municipal plastic waste and 2 Mt of water. In the 55% and 75% defossilisation scenarios, it can be observed that due to the selection of the plastic waste pyrolysis process, high quantities of byproducts like diesel and vacuum gas oil are produced. These heavy hydrocarbons could be further cracked using heavy-oil cracking technologies[97] or sent to oil refineries for processing as synthetic fuels, which can defossilise other unintended sectors. These options could provide further defossilisation in the cluster but are not included in this study.

The highest percentage of defossilisation (95% scenario) is only achieved by removing the naphtha cracker (see SI Figure S22 and Figure 5), as the refinery inputs like pygas or reformate can only be curtailed by shutting down the unit. The second major change observed in the technology portfolio is that, only in the 95% defossilisation scenario, the model deploys water electrolysers for hydrogen production, while in the other scenarios, the cluster still operates with the fossil-based steam methane reformer. This is because the plastic waste based processes require comparatively less additional hydrogen, due to the better C:H ratio of 1:2 in the plastic waste feedstock. For instance, the methanol to aromatics and the plastic waste pyrolysis units in the 55% and 75% scenarios need around 49 kt hydrogen compared to the reference case production of 114 kt. Thus, the existing hydrogen plant in the cluster could absorb the new hydrogen demand in these defossilisation scenarios.

In the 95% defossilisation scenario, the CBB production of ethylene and propylene is significantly higher than in the reference case (see Figure 5 and SI Figure S18). The production of ethylene and propylene increases by 2.7 and 5.3 times, respectively, compared to current production processes. This is due to the difference in the ethylene-to-propylene production ratio of the naphtha cracker in the reference case (equal to 0.6) and the methanol-to-olefin plants in Case 2 (1.3), leading to a high overshoot in propylene production. This effect is not present in the 55% and 75% scenarios, as olefins are produced using plastic waste pyrolysis followed by the existing naphtha cracking process, resulting in a similar share of olefins as in the reference case. Regarding aromatics production, this overshoot is not observed for benzene and/or p-xylene productions (see Figure 5), even though the benzene to p-xylene ratio is 1 and 0.55 for the reference case and Case 2, respectively (i.e., more p-xylene is produced in the ACS case than in the reference case). This is because, in the ACS case, benzene can be produced from both the methanol-to-aromatics and methanol-to-olefin plants, and the model selects a combination of these technologies to fulfil the benzene demand. Such a technology combination is selected because the CAPEX of the methanol-to-olefin process is around 2.2 billion EUR, while the CAPEX of the methanol-to-aromatics process is 2.8 billion EUR, to produce 500 kt of benzene. Hence, as in the model it is cheaper to produce benzene via the methanol-to-olefin route, about 50% of the benzene demand is met with the methanol-to-olefins process, and the other 50% is produced with the methanol-to-aromatics process. Although it is cheaper to produce benzene with the methanol-to-olefin process, the methanol-to-aromatics process is selected to meet the demand for xylene. Thus, the methanol-to-aromatics process (the most expensive process) is first selected to meet the xylene demand, which also produces benzene; however, as all the benzene demand is not fully covered, the methanol-to-olefin process (the cheaper process) is deployed to cover the remaining benzene demand. In addition to the target CBB products, significant quantities of light gases like ethane, propane and C4s are also produced in the ACS case (see Figure 5), which could open new synergies and product lines in the petrochemical cluster to improve material utilisation efficiencies.

In terms of the average selling price of each CBB for each defossilisation scenario, Table 4 shows that the plastic waste pyrolysis-based olefins process results on the least price change impact to its selling prices, increasing between 3% and 18% compared to the fossil case, depending on the plastic waste-based process used. The methanol-to-olefin and aromatics processes create a price increase between 60% and 145% based on the amount of fossil-based methanol imported and the ACS-based methanol produced in the cluster (fossil-based methanol at 650 EUR/t is cheaper than the plastic waste-based methanol at 860 EUR/t).

Defossilising the petrochemical cluster results in a notable change in water demand and wastewater production in the cluster (see Figure 3 for Case 1, SI Figure S19 for Case 2 with 55% defossilisation, SI Figure S21 for Case 2 with 75% defossilisation, Figure 5 for Case 2 with 95% defossilisation). Compared to the reference case (2 Mt of water needed for the naphtha steam cracker and steam methane reformer), between 3 to 14 Mt additional water is needed mainly due to the plastic waste steam gasification process. Even for the 95% defossilisation scenario, the water needed for the electrolysis-based hydrogen production process is only 0.3 Mt (to produce 34 kt hydrogen) compared to the 14 Mt required for the steam gasification process. Hence, in Case 2, considerable water stress is created on the cluster due to the steam gasification process. Also, about 4 to 10 times increase in wastewater production is observed in the ACS-based case compared to the reference case. Thus, water recycling will be critical to reduce the water stress due to the use of the selected ACS-based technologies.

In general, the results of this case highlight that the role of methanol in the cluster increases with defossilisation, from 293 kt/y methanol in the reference case to 9.2 Mt/y in the 55% (or 75%) scenario and 26 Mt/y in the 95% defossilisation scenario, where methanol is used as the intermediate chemical for olefins and aromatics production.

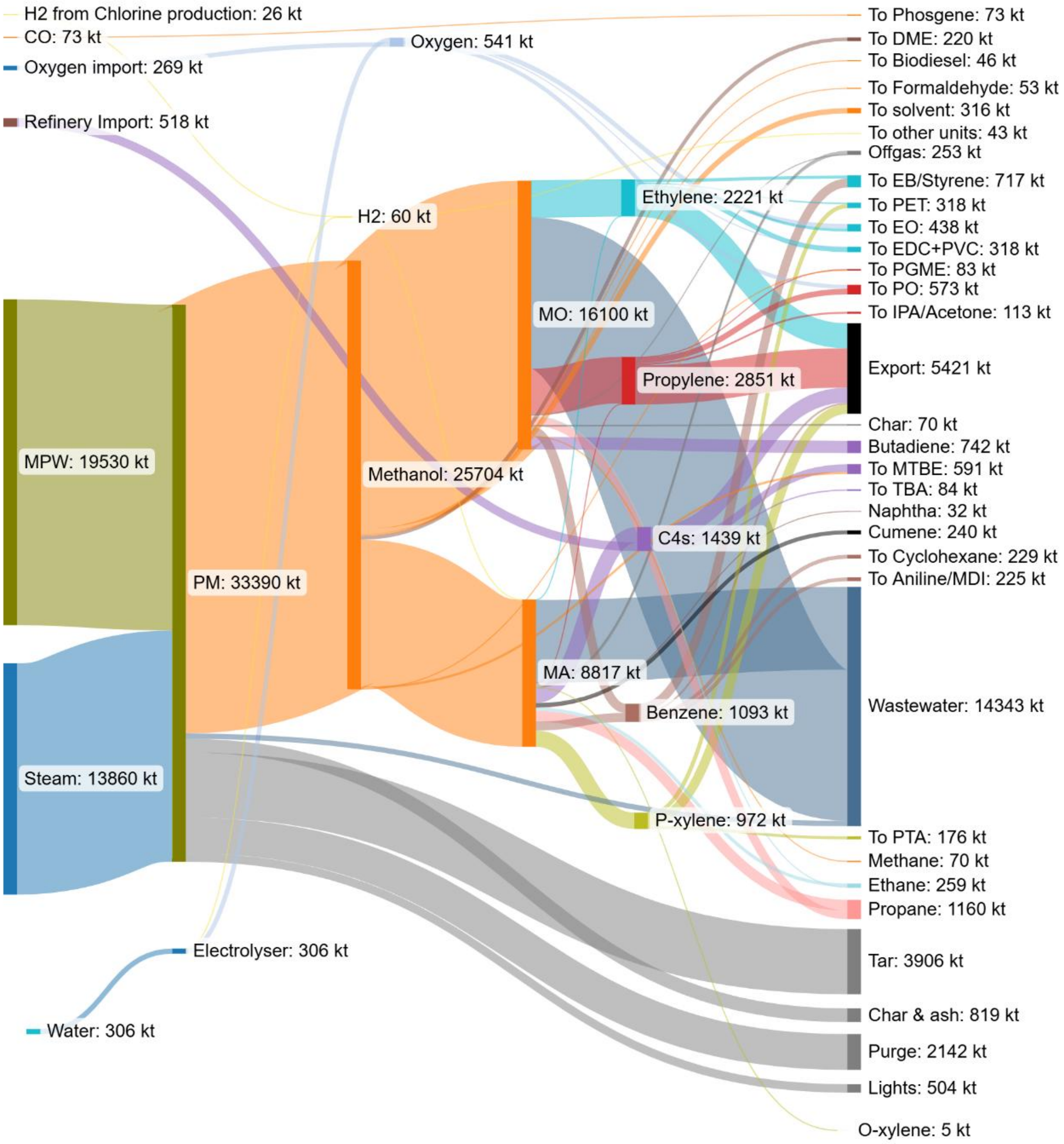

Figure 5. Sankey diagram of mass flows per year for the selected ACS-based processes in Case 2 and 95% defossilisation target (Abbreviations: PM- plastic waste to methanol, MA- methanol to aromatics, VGO- vacuum gas oil, SPW- sorted plastic waste, MPW- municipal plastic waste, EO- ethylene oxide, EDC- ethylene dichloride, DME- dimethyl ether, PVC- polyvinyl chloride, PET- polyethylene terephthalate, EB- ethylbenzene, PO- propylene oxide, PGME- propylene glycol methyl ether, IPA- iso-propyl alcohol, MTBE-methyl tert-butyl ether, TBA- tert-butyl alcohol, MDI- methylene diphenyl diisocyanate, PTA- purified terephthalic acid, SMR- steam methane reformer)

Table 4. portfolio of technologies, CAPEX penalty, mass flows, energy flows and average minimum selling price for Case 2 (Defossilisation without feedstock limitations). The negative sign refers to heat production and positive sign refers to cooling, heating or electricity needs (Abbreviations: SMR: steam methane reformer, NSC: naphtha steam cracker, PM: plastic waste to methanol, PLTP: plastic waste low temperature pyrolysis, MO: methanol to olefin, MA: methanol to aromatics, WE-S: water electrolysis-small, SPW: sorted plastic waste, MPW: municipal plastic waste, CBB: chemical building block, LLPS: Low-low pressure steam, LPS: Low pressure steam, MPS: Medium pressure steam, HPS: High pressure steam, HHPS: High-high pressure steam, HT: High temperature, CW: cooling water)

Defossilisation target	**Technologies (number of units)**	**CAPEX penalty (Billion EUR)**	**Fossil feedstocks (kt/y)**	**Alternative feedstocks (kt/y)**	**Energy needed or produced (PJ/y)**	**CBB production (kt/y)**	**Average minimum selling price (EUR/t)**
55%	Hydrogen: 1 SMR Methanol: 14 PM + Fossil methanol import Naphtha: 2 PLTP + Fossil naphtha import Olefin: 1 NSC Aromatics: 1 MA	10.8	CO:73 Methanol: 3489 Propylene: 24 C4: 518 Naphtha: 600 Pygas: 335 Reformate: 375 Natural gas: 315	CO_2: 0 Biomass: 0 SPW: 10000 MPW: 4340	LLPS: 0 LPS: 11 MPS: -24 HPS: -76 HHPS: -1.5 HT: 38 Electricity: 23 CW: 91	Ethylene: 811 Propylene: 540 Benzene: 1156 P-xylene: 972	Ethylene: 1107 Propylene: 1157 Benzene: 1434 P-xylene: 2445
75%	Hydrogen: 1 SMR Methanol: 23 PM Naphtha: 2 PLTP + Fossil naphtha import Olefin: 1 NSC Aromatics: 1 MA	14.5	CO: 73 Methanol: 0 Propylene: 24 C4: 518 Naphtha: 600 Pygas: 335 Reformate: 375 Natural gas: 315	CO_2: 0 Biomass: 0 SPW: 10000 MPW: 7130	LLPS: 0 LPS: 27 MPS: -37 HPS: -81 HHPS: -1.5 HT: 61 Electricity: 30 CW: 114	Ethylene: 811 Propylene: 540 Benzene: 1156 P-xylene: 972	Ethylene: 1113 Propylene: 1184 Benzene: 1535 P-xylene: 2679
95%	Hydrogen: 2 WE-S Methanol: 63 PM Naphtha: 0 Olefin: 7 MO Aromatics: 1 MA	33	CO: 73 Methanol: 0 Propylene: 0 C4: 518 Naphtha: 0 Pygas: 0 Reformate: 0 Natural gas: 0	CO_2: 0 Biomass: 0 SPW: 0 MPW: 19531	LLPS: 0 LPS: 146 MPS: -91 HPS: -39 HHPS: 0 HT: 158 Electricity: 65 CW: 242	Ethylene: 2221 Propylene: 2851 Benzene: 1093 P-xylene: 972	Ethylene: 2512 Propylene: 2376 Benzene: 2072 P-xylene: 2707

3.3 Case 3 (Defossilisation with limited feedstock availability)

In Case 3, the solutions in the Pareto front only reached 55% defossilisation (see Figure C2 in Appendix C) due to ACS feedstock limitations, compared to the 95% defossilisation reached in Case 2. A combination of ACS and fossil-based feedstocks became necessary to meet the CBB demand in the cluster, when the alternative feedstock is limited (see Table 5). To achieve 55% defossilisation, the CAPEX penalty in Case 3 is 2.3 billion EUR higher compared to the 95% defossilisation scenario in Case 2 (see Figure 6 and SI Figure S27 for the detailed breakdown of CAPEX penalty). Around 48% of the CAPEX penalty is due to the installation of water electrolysers required for hydrogen production. Due to plastic waste feedstock limitation, around 782 kt/y of hydrogen is required in Case 3 compared to 60 kt/y in the 95% defossilisation scenario in Case 2. Furthermore, in Case 2, 63 plastic waste -based methanol plants are installed, while in Case 3, only 6 use plastic waste and the rest of the methanol demand is met by other routes (9 plants using biomass and 3 plants using CO_2 as feedstock). Because of the use of hydrogen-based options, compared to Case 2 and as seen in Figure 6, an additional CAPEX is mainly needed for green hydrogen production. The removal of existing fossil-based technologies did not cause a significant contribution to the CAPEX penalty, as only 6% of the total CAPEX penalty is due to the removal of existing technologies in Case 3.

The electricity consumption is also significantly changed; the electricity demand needed to achieve 55% defossilisation in Case 3 is 3 times higher compared to 95% defossilisation scenario in Case 2 and 28 times higher than the current consumption in the reference cluster (see Figure 7 and SI Figure S28 for detailed breakdown). In terms of feedstock (check Figure 8 and SI Figure S25 for a detailed breakdown of carbon feedstock), compared to the reference case, Cases 2 and 3 need approximately twice as much alternative carbon for defossilisation due to the lower energy densities, and higher byproduct or waste production in the ACS-based processes. Water demand is 1.7 times lower in Case 3 than the 95% defossilisation scenario in Case 2 (and 4 times higher than the reference case). The water demand for 95% defossilisation scenario in Case 2 is higher than the 55% defossilisation scenario in Case 3 due to higher need of a gasifying agent to produce more methanol to achieve higher defossilisation. The water needed in Case 3 is higher than the reference case due the higher steam dilution required in gasification compared to the naphtha cracker (i.e., steam/carbon feedstock ratio of 1 and 0.5 respectively, see SI Figure S26 for a detailed comparison of water demand in the three cases).

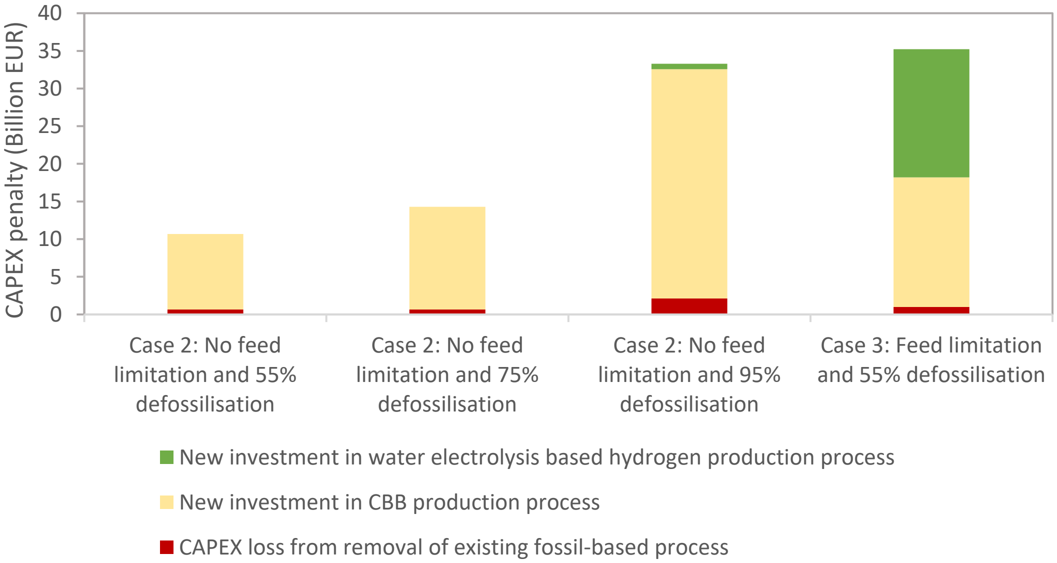

Figure 6. Comparison of the CAPEX penalty between Cases 2 and 3.

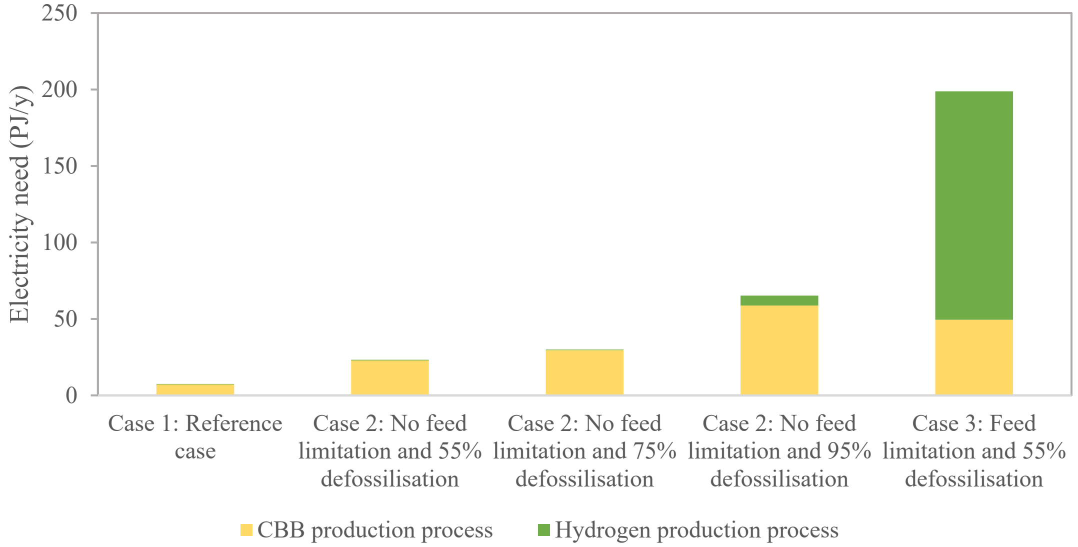

Figure 7. Comparison of the electricity needed in the different cases and scenarios.

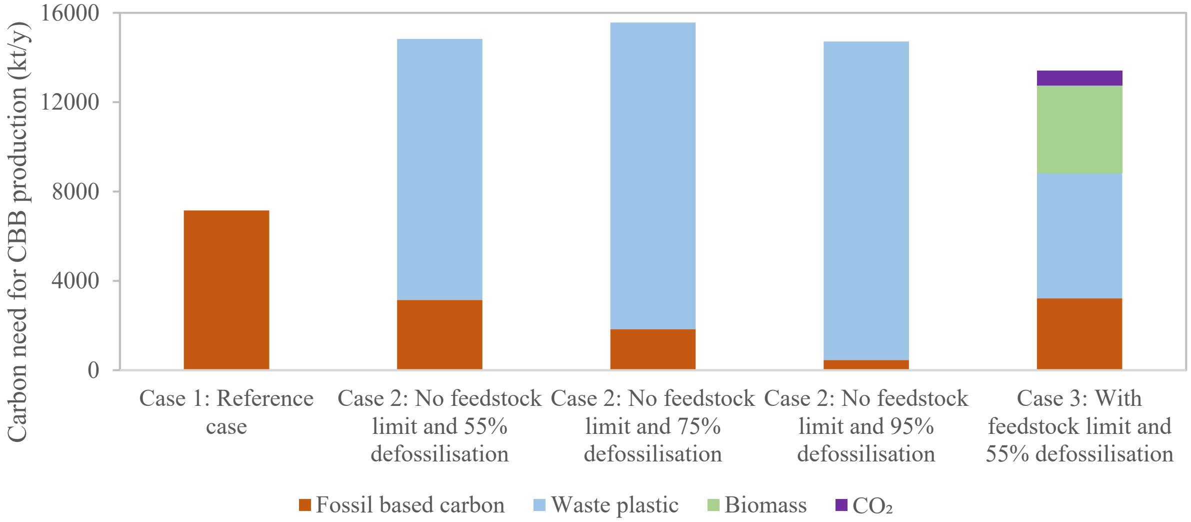

Figure 8. Comparison of carbon needed for CBB production in the different cases and scenarios.

In Case 3, when the limit of 5 Mt/y of sorted plastic waste is included in the model as a constraint, only one plastic waste pyrolysis unit is selected, and thus about 60% of the naphtha needed is still from fossil-based origin (as seen in Figure 10). The olefin production is only partially defossilised and CBB production remains dependent on fossil-based feedstock to meet the demand of ethylene and propylene in the cluster. Similarly, with limited availability of CO_2, biomass and municipal plastic waste for methanol production, the model prefers to defossilise the aromatics process over the olefin process (see in SI Figure S24 the technology portfolio selected for Case 3 and 55% defossilisation). This is because more than 50% of the embedded carbon in the CBB is accounted by benzene and p-xylene (see in Figure 9 and SI Figure S16 the embedded carbon distribution in cluster products). Therefore, defossilising aromatics creates the highest embedded carbon impact in the cluster. A total of 9.2 Mt/y methanol is needed for the methanol-to-aromatics plant, however, only 7.4 Mt/y methanol can be produced due to the ACS feedstock limitations. Hence, 20% of the methanol required by the cluster is imported. Thus, in Case 3, the CBB production of olefins and aromatics is only partially defossilised, and the cluster still depends on fossil-based feedstocks to meet the CBB demand.

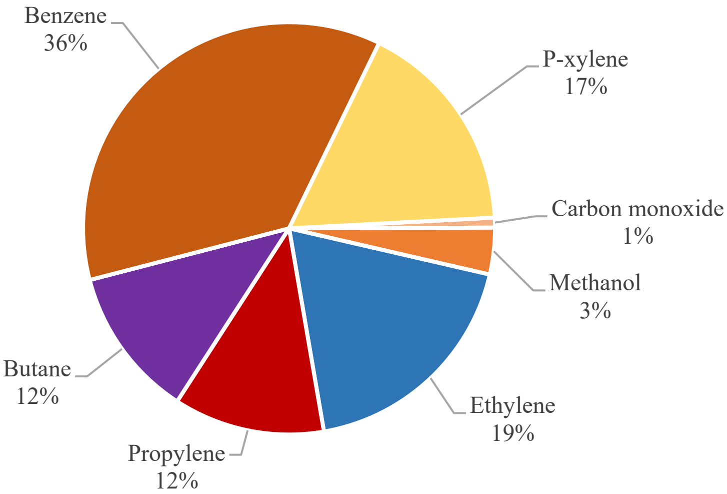

Figure 9. Embedded carbon distribution in the reference case petrochemical cluster (Note: the chart shows that benzene is the highest embedded carbon contributor, followed by ethylene, p-xylene, propylene, butane, methanol and carbon monoxide, respectively)

In Case 3, the average selling price of CBB increased by 10%-40% for olefins and by 175%-330% for aromatics. The price change is lower for olefins than aromatics, as the most price-competitive plastic waste pyrolysis-based process is selected over the methanol-to-olefins route. The price change of aromatics is higher in Case 3 when compared to all scenarios in Case 2 due to the higher average methanol price (1568 EUR/t in Case 3 compared to 780-860 EUR/t in Case 2). This is because in Case 2, 100% of the methanol is obtained from the cheaper fossil-based and plastic waste-based routes, while in Case 3, 53% of the methanol is obtained from the more expensive CO_2 and biomass-based routes.

Note that the technology portfolios in this chapter have been optimised for minimising CAPEX penalty based on the current CAPEX and efficiencies of the selected ACS-based processes. For example, it was assumed that a 30% stack replacement[115] is required for the CO_2 electrolyser every 5 years[114]. The optimisation method used in the study does not take into account the future technology improvements for the ACS-based processes, which could potentially change the technology portfolio over time.

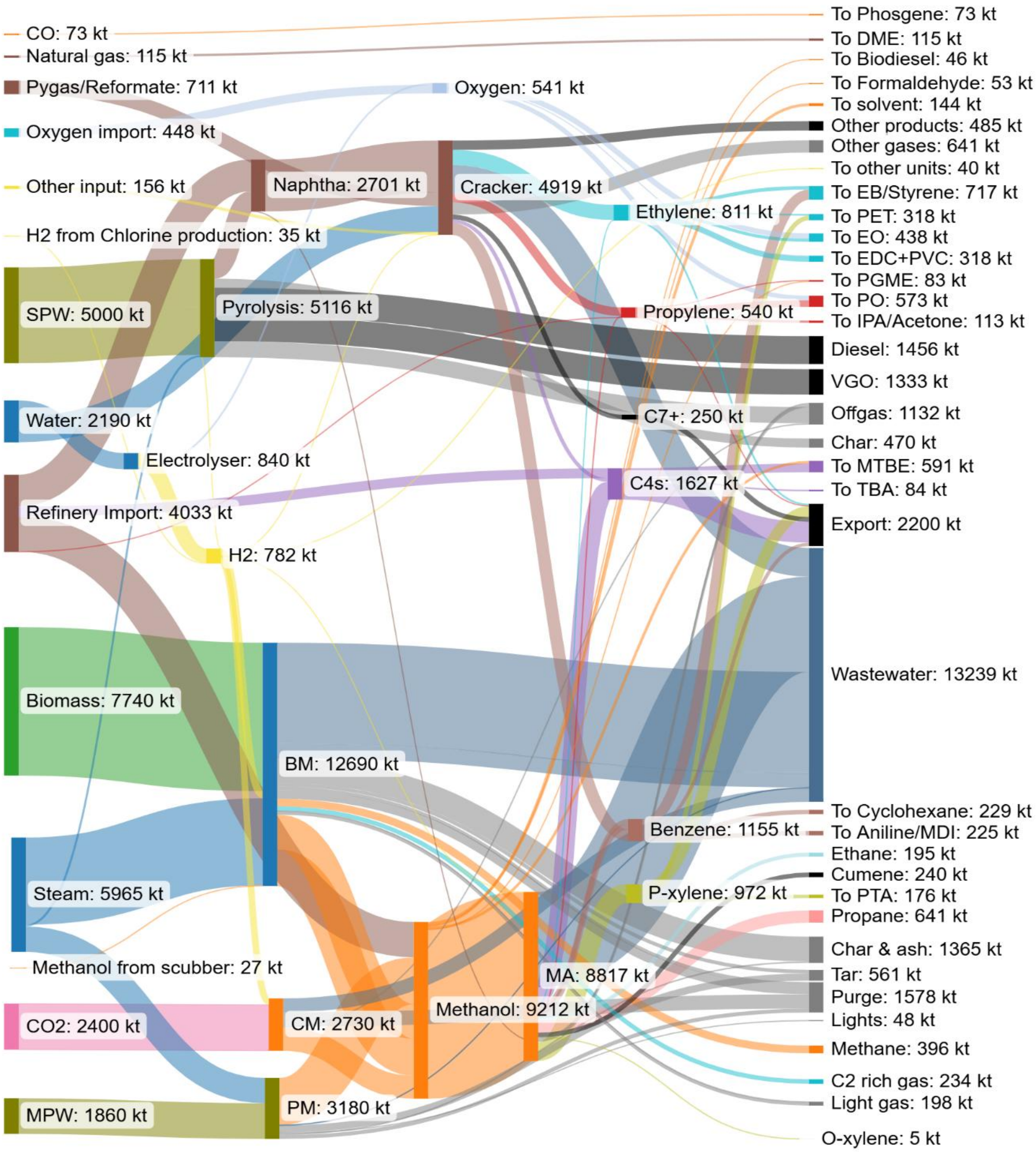

Figure 10. Material flow diagram per year for Case 3 (55% defossilisation considering feedstock limitations). (Abbreviations: BM- Biomass to methanol, CM- CO_2 to methanol, PM- Plastic waste to methanol, MA- Methanol to aromatics, VGO- Vacuum gas oil, SPW- Sorted plastic waste, MPW- Municipal plastic waste, EO- Ethylene oxide, EDC- Ethylene dichloride, DME- Dimethyl ether, PVC- Polyvinyl chloride, PET- Polyethylene terephthalate, EB- Ethylbenzene, PO- Propylene oxide, PGME- propylene glycol methyl ether, IPA- Iso-propyl alcohol, MTBE-Methyl tert-butyl ether, TBA- Tert-butyl alcohol, MDI- Methylene diphenyl diisocyanate, PTA- Purified terephthalic acid, SMR- Steam methane reformer).

Table 5. Portfolio of technologies, CAPEX penalty, mass flows, energy flows and average minimum selling price for Case 3 (Defossilisation with feedstock limitations). Note: The negative sign refers to heat production and positive sign refers to cooling, heating or electricity needs. (Abbreviations: NSC: naphtha steam cracker, BM: biomass to methanol, CM: CO_2 to methanol, CO: CO_2 to ethylene, PM: plastic waste to methanol, PLTP: plastic waste low-temperature pyrolysis, MA: methanol to aromatics, WE-S: water electrolysis-small, WE-L: water electrolysis-large, SPW: sorted plastic waste, MPW: municipal plastic waste, CBB: chemical building block, LLPS: Low-low pressure steam, LPS: Low pressure steam, MPS: Medium pressure steam, HPS: High pressure steam, HHPS: High-high pressure steam, HT: High temperature, CW: cooling water)

Defossilisation	**Technologies (number of units)**	**CAPEX penalty (Billion EUR)**	**Fossil feedstocks (kt/y)**	**Alternative feedstocks (kt/y)**	**Energy needed or produced (PJ/y)**	**CBB production (kt/y)**	**Average minimum selling price (EUR/t)**
55%	Hydrogen: 6 WE-S + 6 WE-L Methanol: 9 BM + 6 PM + 3 CM + Fossil methanol import Naphtha: 1 PLTP + Fossil naphtha import Olefin: 1 NSC Aromatics: 1 MA	35.3	CO: 73 Methanol: 1760 Propylene: 24 C4: 518 Naphtha: 1650 Pygas: 335 Reformat: 375 Natural gas: 115	CO_2: 2400 Biomass: 7741 SPW: 5000 MPW: 1860	LLPS: 3 LPS: -21 MPS: -13 HPS: -61 HHPS: -1.5 HT: 15 Electricity: 199 CW: 141	Ethylene: 811 Propylene: 540 Benzene: 1156 P-xylene: 972	Ethylene: 1169 Propylene: 1430 Benzene: 2437 P-xylene: 4759

4. Conclusions

Defossilising the production of chemical building blocks (CBB) like methanol, olefins and aromatics, using alternative carbon sources (ACS) like CO_2, biomass and plastic waste, will be crucial for the transition of the chemical industry. Previous studies have pointed out that limited availability of ACS feedstocks will impact the technology portfolio selected for defossilising the CBB production. However, the impact of the ACS feedstock availability on the technology portfolio and the performance of a brown-field petrochemical cluster has not been studied in depth. In this research, to analyse and quantify the impact of feedstock availability on the performance of a cluster, three cases were considered mimicking the situation in the Port of Rotterdam: a reference case representing the current petrochemical cluster (Case 1), a case without limits on ACS availability (Case 2) and a case with limited ACS availability (Case 3). The technology portfolio in each case was selected based on an optimisation model that minimises fossil feedstock usage in the cluster and maximises the use of existing assets in the cluster to achieve different percentages of defossilisation compared to the reference case.

The results show considerable changes in the cluster performance in terms of carbon feedstock, byproduct production, CAPEX, electricity, water demand and price change for Cases 2 and 3 compared to Case 1. In Case 2, when sufficient ACS were considered available, the plastic waste pyrolysis (i.e., pyrolysis with steam cracking) and the plastic waste gasification-based processes (i.e. gasification with syngas to methanol followed by methanol to olefin and methanol to aromatics) appeared to be the preferred choices, due to their low CAPEX and low hydrogen needs. Up to 95% defossilisation could be achieved in Case 2 for the production of CBB, which required around 19.5 Mt/y of plastic waste (more than three times the current total plastic production in the Netherlands). This high ACS need was mainly due to the large byproduct production, such as offgas and heavy hydrocarbons (between 6 Mt/y and 12 Mt/y). A CAPEX penalty of approximately 33 billion EUR was incurred to achieve 95% defossilisation in Case 2, with plastic waste conversion to methanol intermediate accounting for about 76% of this CAPEX penalty. The electricity demand rose 9 times for the 95% defossilisation scenario in Case 2 compared to Case 1 (i.e., 65 PJ/y, which is equivalent to 32% of total renewable energy production in the Netherlands in 2024) due to the high pressure needed in the methanol production process, particularly for syngas pressurisation and recycling. The water demand in the 95% defossilisation scenario in Case 2 was about 7 times higher compared to Case 1, mainly due to the steam gasification process used in the methanol production process. The relevance of methanol as an intermediate for olefin and aromatics production increased in the 95% defossilisation scenario in Case 2, as approximately 26 Mt/y of methanol was required compared to the 293 kt/y in Case 1. Thus, Case 2 shows that plastic waste-based methanol to olefins and aromatics technologies are preferred routes because of the multi-product nature, comparatively lower CAPEX and lower hydrogen needs for defossilising petrochemical clusters. However, a substantial amount of feedstock is required.

In Case 3, the maximum defossilisation obtained was 55% of the CBB production when considering ACS feedstock limits of 3 Mt/y CO_2, 8 Mt/y biomass and 7 Mt/y plastic waste. In this case, olefin production was partially defossilised by using synthetic naphtha from a plastic waste-based pyrolysis process; aromatics production was defossilised by using the methanol-to-aromatics process, and hydrogen production was defossilised by using water electrolysis. A comparison of the cases showed that high quantities of external hydrogen were required in Case 3, particularly for biomass and CO_2 feedstocks. Due to the high hydrogen demand, the electricity demand was as high as 28 times that of Case 1 (199 PJ/y, equivalent to the total renewable energy production in the Netherlands in 2024). Furthermore, in Case 3, the cluster will incur around 35 billion EUR in investment to defossilise up to 55% of the cluster, which is about 18 times the CAPEX of the fossil-based CBB production plants. In Case 3, about 48% of the CAPEX penalty is due to the water electrolysis process for green hydrogen production. Case 3 highlights that in the case with limited ACS feedstock, the cluster operated by combining fossil-based and ACS-based technologies, namely with 42% of carbon need met with plastic waste, 29% met with biomass, 24% met with fossil sources and 5% met with CO_2. In such a case, assumptions about hydrogen production can significantly alter the required investment, as it accounts for about 50% of the CAPEX penalty.

This research reaffirms that there is no silver bullet technology to defossilise the production of chemical building blocks and underscores the critical need to balance technological choices with realistic assessments of ACS feedstock availability to ensure a sustainable and economically viable transition for the chemical industry. Future research can further explore the impacts of improving the defossilisation potential in the ACS feedstock limited case by valorising and recycling byproducts, offgases and wastewater.

7. Conclusion and perspectives

Chapter specific nomenclature & symbols

Nomenclature

ACS	Alternative carbon source
CBB	Chemical building blocks
KPI	Key performance indicator
LCA	Life cycle analysis
PoR	Port of Rotterdam
RQ	Research question
R&D	Research & development
TRL	Technology readiness level

Symbols

kt/y	Kilotonne per year
Mt/y	Million tonne per year
PJ	Petajoules

1. Introduction

This chapter summarises the research outputs and answers the main research question proposed in Chapter 1. The chapter ends by discussing the limitations of the work and provides recommendations for future research.

This dissertation explored the process and cluster level impacts of using alternative carbon sources (ACS) to produce chemical building blocks (CBB) in existing petrochemical clusters. The overarching motivation is to reduce dependency on fossil carbon feedstock by replacing it with biomass, CO_2 or plastic waste. In this thesis, one promising technology from each ACS feedstock was selected for each CBB. The selected technologies were subsequently modelled in Aspen Plus with design, operating capacities and process complexities similar to those found in the current CBB production plants in the Port of Rotterdam (PoR). The technologies were then assessed using key performance indicators (KPIs) at both process and cluster levels. Finally, this thesis evaluated the technology portfolio required for defossilising the production of CBB (methanol, ethylene, propylene, benzene, p-xylene) and examined how limitations in ACS feedstock availability could affect the design and performance of a defossilised brownfield petrochemical cluster.

2. Research results

The overarching aim of the thesis was to understand

the impacts of defossilising the production of chemical building blocks in existing petrochemical clusters.

The main research question (RQ) was:

How can the use of alternative carbon sources affect the production of chemical building blocks in existing petrochemical clusters?

To answer this question, three sub-research questions were proposed. In this section, each question is answered using key results and conclusions from Chapters 2 to 6. Then, an overall conclusion is made to answer the main research question.

SRQ-1: How to screen promising ACS-based process routes at different TRLs for the production of chemical building blocks? (Chapters 2 and 3)

With the need to defossilise the petrochemical sector, many possible process routes that use ACS are being developed (see Table 1). For instance, to produce ethylene, more than sixty-five different ACS-based process routes were identified in the literature. These multiple options are at different levels of development, making the selection of promising process route a complex task.

Table 1: Number of 3-step process routes identified to produce chemical building blocks from ACS feedstocks

Chemical building block	CO_2	Biomass	Plastic waste	Intermediate
Methanol	11	15	6	Carbon monoxide, Carbon dioxide, Methane
Ethylene	24	24	17	Carbon monoxide, Carbon dioxide, Methane, Methanol, Methyl halide, Ethane, Ethanol, Acetylene, Dimethyl ether, Naphtha

Propylene	22	21	15	Carbon monoxide, Carbon dioxide, Methanol, Methyl halide, Ethanol, Ethylene, Dimethyl ether, Propane, Propanol, Glycerol, Naphtha
Benzene and P-xylene	16	14	8	Carbon monoxide, Carbon dioxide, Methane, Methanol, Acetylene, Toluene, Xylene, Naphtha

As described in Chapters 2 and 3, a screening methodology based on a stage-gate concept was developed to select promising ACS technologies to further study in this thesis. The method used ideal stoichiometric reactions and thermodynamic state functions at standard temperature and pressure conditions.

The assessment revealed that the C:H:O ratio of the ACS feedstocks played a major role in the technical performance of the process because higher oxygen content in the feedstock results in lower carbon utilisation efficiencies or higher hydrogen need. For example, given that the oxygen content of CO_2, biomass and plastic waste are 73 wt%, 49 wt% and 0 wt% respectively, CO_2 required the highest energy input for oxygen removal through hydrogenation or electrochemical reduction for CBB production. As seen in Table 2, plastic waste has a similar C:H:O composition compared to the fossil fuel-based feedstocks, and consequently, plastic waste-based technologies scored better compared to biomass and CO_2 in the screening methodology. This was because plastic waste-based technologies required the least energy and material input due to the 0 wt% oxygen content. The relevance of oxygen content in the ACS feedstock was particularly relevant due to the non-oxygenated target products like ethylene, propylene, benzene and xylene considered in the study.

Table 2: Carbon, hydrogen and oxygen content of different feedstocks

Different feedstocks		**Carbon content (mass %)**	**Hydrogen content (mass %)**	**Oxygen content (mass %)**
Fossil based	Naphtha	85%	15%	0%
	Natural gas (Methane)	75%	25%	0%
ACS based	$Carbon\ dioxide\ (CO_2)$	27%	0%	73%
	Biomass ($-C_6H_{10}O_5-$)	45%	6%	49%
	$Polyethylene\ (-C_2H_4-)_n$	86%	14%	0%

As discussed in Chapter 3, technology screening methodologies in the literature have overlooked the potential impact of hydrogen origin. In most cases, hydrogen availability is implicitly assumed, and its origin is simply cited, and it is often assumed to be 'green'. However, the origin and availability of hydrogen depend on the geographical location and strategic decisions taken, possibly even outside the boundaries of the problem under study. We examined four types of hydrogen origins to explore the extent which hydrogen source impacts the selection of ACS-based technologies to produce ethylene (Chapter 3): process hydrogen (embedded in the feedstock), green hydrogen, blue hydrogen (on-site production) and hydrogen import. We used carbon utilisation efficiency, electricity needs, heat needs and heat production as key performance indicators.

The results showed that assumptions regarding the hydrogen origin have a significant impact on the ranking of technologies. For example, by assuming that hydrogen was imported (i.e., without further consideration of its origin), the screening methodology would identify exothermic technologies based on hydrogenation of CO_2-to-methanol and oxygen gasification of biomass or plastic waste as favourable routes to be further examined. If, however, the production of hydrogen was considered to be onsite, direct electrochemical reduction, biomass steam gasification and plastic waste pyrolysis performed better than the exothermic routes mentioned above, in terms of material and energy efficiencies. This is because the material and energy penalties of the highly endergonic hydrogen production processes were outside the scope in the hydrogen import case. This research highlights how assumptions on hydrogen availability and origin, which tend to be made earlier in the scoping phase, can significantly change the R&D portfolio. This is especially the case when assessing CO_2-based routes.

SRQ-2: What are the techno-economic impacts of using ACS-based technologies for the production of chemical building blocks in existing petrochemical clusters? (Chapters 4 and 5)

Considering hydrogen origin, the selected technologies to produce CBB in the modelled cluster were direct electrochemical reduction, steam gasification, methanol-to-olefins or aromatics, Fischer-Tropsch and pyrolysis processes, as outlined in Figure 1.

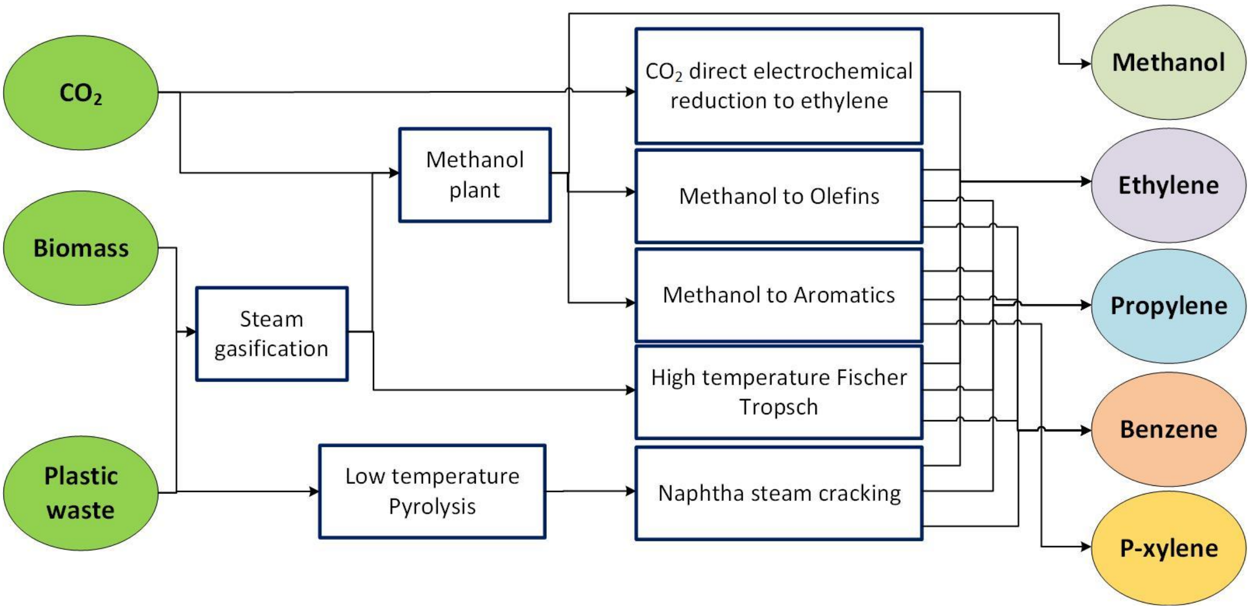

Figure 1: Overview of selected technologies identified through the stage-gate screening methodology for the production of chemical building blocks from ACS feedstocks.

Replacing fossil-based processes in interconnected industrial clusters can impact upstream supply chains, downstream units, energy islands, waste treatment plants, and change the overall performance or cause lock-in situations at the cluster level. This, however, has been overlooked in the literature. Chapters 4 and 5 evaluated the impacts of replacing fossil-based olefin and aromatics production in an existing industrial cluster with biomass-, CO_2- and plastic waste-based processes. We evaluated the performance of the ACS-based production routes at both process and cluster levels by assessing changes in mass, energy, prices, CO_2 emissions and water demand. The results show that due to the significant differences in product distribution, energy needs and waste generation, a significant reconfiguration of the petrochemical cluster will be needed in terms of mass and energy flows. Therefore, defossilising the production of chemical building blocks in existing petrochemical clusters cannot be approached as a plug-and-play situation.

In Chapter 4, process and cluster level impacts of defossilising olefin production in an existing petrochemical cluster were analysed. At process level, the main challenges to defossilise olefins were (i) access to large quantities of renewable electricity at cheap prices, particularly for hydrogen production, and (ii) the large investment costs of ACS-based processes compared to fossil fuel-based technologies. For instance (as seen in Table 3), to produce 900 kt/y of ethylene (which is the current production in PoR), the CO_2-based direct electrochemical reduction route required around 250.3 PJ/y electricity, and 47 billion EUR of CAPEX investment compared to the current technology (naphtha steam cracker), which requires around 7.3 PJ/y electricity and 1 billion EUR of CAPEX investment.

Table 3: Comparison of process level KPIs for the reference and ACS-based technologies to produce 900 kt/y ethylene

	Carbon source			
	Naphtha	**CO_2**	**Biomass**	**Plastic waste**

	Reference case	Direct electrochemical	Methanol-to- olefin	Fischer Tropsch + methanol - to- olefin	Methanol - to- olefin	Pyrolysis + cracking	Methanol -to-olefin
Electricity need (PJ)	7.3	250.3	469.6	351.4	237.9	18.3	19.1
CAPEX (Billion EUR)	1.13	47.4	53.2	38.3	37.9	4.6	8.2

The higher CAPEX of CO_2-based technologies was due to the assumed electrolyser cost (1059 EUR/kW and 1500 EUR/kW for PEM type water and CO_2 electrolysers, respectively) and the electrolyser lifespan (9 years for water electrolyser and 5 years for CO_2 electrolysers). The scenario analysis showed that CO_2-based technologies could become cost competitive with current fossil-based technologies with an electricity price of 11 EUR/MWh, an electrolyser (water electrolyser and CO_2 electrolyser) cost of 580 EUR/kW and a lifespan of 25 years. Among the three alternative carbon sources, plastic waste-based ethylene showed the lowest electricity requirements (18-19 PJ/y) and CAPEX investment (5-8 billion EUR). In general, plastic waste-based technologies showed a better performance than the biomass and CO_2 based technologies, due to their better C/H ratio of the feedstock, leading to lower external hydrogen demand and higher olefin yields.

At the cluster level, replacing the naphtha cracker with ACS-based technologies for olefins production presents significant challenges. This is mainly due to differences in product profiles and the need for substantial changes in electricity, water, and waste treatment infrastructure. On average, the ACS-based processes needed 5 to 10 times more electricity and water per unit of ethylene produced, as seen in Table 4. The significant difference in utility needs shows that a complete overhaul of the energy and utility plants will be required to integrate the ACS-based processes into the cluster.

Table 4: Comparison of cluster level KPIs for the reference and ACS-based technologies to produce 900 kt/y ethylene

	Carbon source						
	Naphtha	CO_2		Biomass		Plastic waste	
	Reference case	Direct electrochemical	Methanol to olefin	Fischer Tropsch + methanol to olefin	Methanol to olefin	Pyrolysis + cracking	Methanol to olefin
Propylene/ ethylene (kg/kg)	0.57	0	1.27	0.99	1.27	0.57	1.27
Electricity/ ethylene (MJ/kg)	8	254	498	389	253	20	20
Water/ ethylene (kg/kg)	1.7	6.8	18.7	22.9	16.8	2.7	4.2
Wastewater/ ethylene (kg/kg)	1.9	4.1	8.7	23.4	16.9	1.9	6.5

Ripple effects on the structure of the cluster due to defossilisation were seen because of the difference in the product-to-byproduct ratio (i.e., mainly for propylene, offgases and heavy hydrocarbons in the ACS cases). This also creates “a shifting of burden” to outside the cluster for the production of byproducts, resulting in a net increase of the fossil fuel consumption (as observed in Chapter 4). This was particularly the case for the CO_2-based direct electrochemical reduction process to produce ethylene, in which no propylene is produced. As a result, propylene production was imported, introducing logistical and environmental challenges (if the propylene were fossil-based).

The different ACS-based technologies resulted in lower fossil carbon content and notable price changes along the value chains. For example, a +134% price change in ethylene as a consequence of using ACS processes would result on a 97% increase in price of polyvinyl chloride and a 34% price increase in polyethylene terephthalate. The different impacts along the value chain are due to differences in CBB needed in the production processes, reference prices and process yields. Among the different olefin value chains polyvinyl chloride and acetone appeared as the most impacted both in terms of reaching the highest defossilisation and highest price impacts. This is because 80% and 100% of the embedded carbon in polyvinyl chloride and acetone originates from ethylene and propylene, respectively.

In Chapter 5, the process and cluster level impacts of defossilising aromatics production in an existing petrochemical cluster were analysed. At process level, similar to the findings in Chapter 4, the high requirement for renewable electricity and investment costs of ACS-based processes were the main challenges (Table 5). Among the ACS-based routes, the plastic waste-based methanol-to-aromatics route appeared as the most competitive with the lowest impact at the cluster level.

Table 5: Comparison of process level KPIs for the reference and ACS based technologies to produce 1000 kt/y benzene

	Carbon source			
	Naphtha	**CO_2**	**Biomass**	**Plastic waste**
	Reference case	**Methanol-to-aromatics**	**Methanol-to-aromatics**	**Methanol-to aromatics**
Electricity need (PJ)	0.7	1152	585	51
CAPEX (Billion EUR)	0.6	134	97	24

At the cluster level (Table 6), the main differences among the processes were found in high xylene production, off gas production, electricity and water requirements, and waste treatment infrastructure. The significant difference in utility needs was mainly due to the high hydrogen need and higher pressure requirements for the methanol production process compared to the reference case. The higher water demand was due to the water electrolysis and steam gasification process required to produce the syngas needed for the methanol production process. About 80%-90% of the electricity and CAPEX was accounted by the ACS to methanol production process. Thus, for the ACS-based aromatics process, the techno-economic performance of the methanol production process played both a key role at the process and cluster level.

Table 6: Comparison of cluster level KPIs for the reference and ACS based technologies to produce 1000 kt/y benzene

	Carbon source			
	Naphtha	**CO_2**	**Biomass**	**Plastic waste**
	Reference case	**Methanol to aromatics**	**Methanol to aromatics**	**Methanol to aromatics**
Xylene/ benzene (kg/kg)	0.5	1.1	1.1	1.1

Electricity/ benzene (MJ/kg)	1	1076	547	47
Water/ benzene (kg/kg)	1.0	25.6	23.1	6.5
Wastewater/ benzene (kg/kg)	1.1	12.6	23.3	6.7

Among the different value chains for benzene and p-xylene, cyclohexane and polyethylene terephthalate, will have the highest defossilisation and price impacts, respectively. This is because 80%-100% of the embedded carbon in cyclohexane and polyethylene terephthalate originates from benzene and p-xylene, respectively. Compared to the defossilisation of olefin (chapter-4), the defossilisation of aromatics created the highest change in embedded carbon in the cluster, as aromatics account for over 50% of the embedded carbon in the cluster.

For both ACS-based olefins and aromatics processes, the large electricity need, hydrogen consumption, and waste generation created major environmental consequences like higher water consumption, wastewater generation, and CO_2 emissions (Scope 1 and 2), which, if not addressed properly, could nullify the purpose of defossilising chemical building blocks. Our analysis shows that further improvements in waste valorisation and the integration of renewable energy are required to ensure the climate change impact of ACS-based technologies. ACS-based technologies should therefore be deployed in tandem with renewable energy-based utilities and wastewater recycling plants for the system to be low-carbon and reduce water stress.

SRQ-3: How does the availability of alternative carbon sources affect potential technology portfolios for defossilising the production of chemical building blocks in existing petrochemical clusters? (Chapter 6)

For producing the same quantity of CBB, larger quantities of ACS-based feedstocks will be required compared to fossil-based feedstocks due to the low carbon and hydrogen content of ACS-based feedstocks[53]. The availability of ACS will not only affect the limit up to which a petrochemical cluster can be defossilised, but it also effects the technology portfolio required for CBB production. In our study, we analysed eight ACS-based technologies for CBB production to meet the current demand in an existing cluster mimicking the situation in the Port of Rotterdam, the Netherlands. We optimise the technology portfolio considering two objective functions (i) minimising fossil carbon use and (ii) minimisation of CAPEX penalty (defined as the sum of new investment plus the loss CAPEX due to removing existing assets) in order to limit the change in existing infrastructure. Three cases were

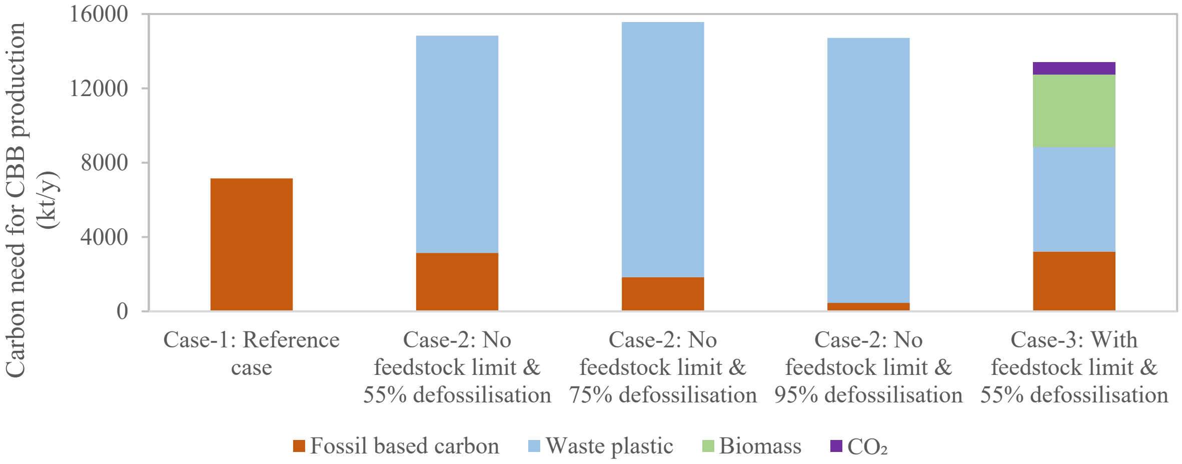

Figure 2: Comparison of carbon sources required for CBB production in the reference and defossilisation cases

explored: a reference case, and two cases defined by availability of ACS feedstocks. One where there would be no limits and another with limited availability.

The comparison of the technology portfolios between the unlimited and limited ACS cases showed a variation of 2 to 8 times in CAPEX penalty, energy estimates and water demand. Achieving a 95% defossilisation rate resulted in a significant capital expenditure (CAPEX) penalty of approximately €33 billion, alongside an electricity demand of 65 PJ per year. This contrasts sharply with the reference case, which required only €2 billion in CAPEX and 7 PJ per year of electricity. Furthermore, water demand in the cluster rose from 2 million tonnes per year in the reference case to 14 million tonnes per year in the defossilisation scenario with unlimited availability of feedstocks, primarily driven by the steam gasification process used to convert plastic waste into methanol via syngas To achieve up to 95% defossilisation for the production of chemical building blocks, about 19.5 Mt/y plastic waste would be required, which is over three times higher than the current plastic production in the Netherlands. When sufficient plastic waste would be available, among the plastic waste-based ACS technologies, the methanol-based process was selected, as methanol could be converted to both olefins and aromatics.

When limitations in feedstocks were included in the model, the maximum defossilisation obtained was 55% of CBB production. This case required around 200 PJ/y electricity, 3 Mt/y of CO_2, 8 Mt/y biomass and 7 Mt/y of plastic waste. Olefin production was partially defossilised using synthetic naphtha from plastic waste-based pyrolysis, aromatics production was defossilised using a methanol to aromatics process, and hydrogen production was defossilised using water electrolysis. The study estimated that around 35 billion EUR of CAPEX penalty will be incurred to defossilise up to 55% of the cluster, which is about 18 times the CAPEX of the fossil-based CBB production plants in the model. The water demand in the cluster increased from 2 Mt/y in the reference case to 8 Mt/y, mainly due to the steam gasification process required for converting plastic waste and biomass to methanol via syngas and hydrogenation of CO_2-to-methanol. Our results indicate that, given ACS feedstock limitations and current demands of (fossil fuel-based) CBB, a combination of ACS and fossil-based technologies will co-exist (as shown in Case 3 of Figure 2). There is no single "silver bullet" process or feedstock that can fully defossilise CBB production; instead, a combination of portfolio of options will be required.

How can the use of alternative carbon sources affect the production of chemical building blocks in existing petrochemical clusters?

A large number of technological options are currently being developed to produce CBB using ACS. From the literature, we identified more than 190 possibilities to produce methanol, olefins and aromatics (as was summarised in Table 1). Selecting promising process routes for implementation is a major challenge for researchers, industries and policy makers. We proposed a screening methodology based on ideal reactions and thermodynamic state functions to select promising technologies from a large number of possibilities. The thermodynamic analysis indicated that due to the differences in the carbon, hydrogen and oxygen content in the ACS, the plastic-based technologies (more similar to fossil fuels compositions) performed techno-economically better, followed by biomass and CO_2-based technologies, respectively. Eight ACS-based technologies were selected using the screening methodology, one for each feedstock and CBB.

The techno-economic analysis at the process level and cluster level of these eight processes showed that, in general, plastic-based technologies performed techno-economically better (in line with the observations in the screening methodology), but this option is highly dependent on feedstock availability. The cluster level analysis showed that the interdependencies between chemical plants through mass and energy with downstream value chains, utilities and waste treatment plants, can lead to unintended cluster impacts. These impacts appeared mainly from differences in feedstock requirements, product distributions and energy flows, showing that defossilising existing petrochemical clusters will not be a plug-and-play situation due to the existing infrastructures like pipes and equipment. Our analysis also showed that current highly integrated clusters need to create new synergies for the ACS-based CBB production processes. Such new material and energy integrations are required; for example, to valorise excess steam, propylene, p-xylene or heavy hydrocarbon production in ACS-based technologies.

ACS feedstock limitation will play a key role in how industrial clusters will develop. The work in this thesis showed that there is no single "silver bullet" process to defossilise the production of CBB, but a combination of ACS and fossil-based technologies will be required. With renewable energy and ACS feedstock limitations of 200 PJ/y, 3 Mt/y CO_2, 8 Mt/y biomass and 7 Mt/y plastic waste, only 55% of the CBB production could be defossilised in the Port of Rotterdam cluster, which showed the magnitude of energy and material required for such a change. The biggest challenge for an existing petrochemical cluster similar to the Port of Rotterdam, with restricted access to land, will be the 5 to 10 times higher electricity and water needs. This shows that either the production capacities need to be downscaled or strategic decisions regarding which chemical to produce in the cluster have to be made. Another option is to import intermediate renewable carbon feedstocks like methanol, pyrolysis oil, ethanol or Fischer Tropsch naphtha into the cluster. However, as these processes are highly energy, CAPEX, and land-intensive processes, this shift may result in increasing environmental impacts outside the Netherlands.

3. Limitations

The research approach employed in this dissertation consisted of process modelling and ex-ante techno-economic impact assessment of the ACS-based cases at both process and cluster levels. The modelling work required the use of several assumptions. The major limitations of this study are:

- Contrary to the reference case where a certain level of verification was possible using the current situation in the Port of Rotterdam; for the ACS-based technologies, as most of them have not been implemented, such verification was not possible. Thus, uncertainty or error propagation analysis at cluster level were not studied due to the low TRL of ACS-based technologies and complexity of the petrochemical cluster. The emphasis was more on the trends, trade-offs rather than absolute impact. However, the data is highly uncertain due to the low TRL and therefore understanding of error propagation, especially at cluster level, will be desirable.
- The analysis in Chapters 4, 5 and 6, show that considerable amounts of by-products are produced by using the ACS-based technologies. For example, plastic pyrolysis process produces significant quantities of heavy hydrocarbons along with naphtha. These byproducts can be further valorised to improve the process economics and to extend defossilisation level. This, however, was not considered in this study.
- The exploratory nature of the research was to understand the system level impacts and due to the complexity, process level optimisation was not done. For example, in heat integration the streams were heated or cooled step-wise using the pre-defined utilities and pinch point analysis was not applied. Thus, the energy calculations could be further optimised.
- The ACS-based processes required around 3 to 5 times more water than the reference case processes. In line with this, the ACS-based processes also produced 3 to 5 times more wastewater than the reference case processes. However, wastewater recycling was not considered in the study to reduce the water demand of the ACS-based processes.
- The source of (renewable) energy was outside the scope of this research and the consequence of that choice is not addressed in the study. The impact of variable renewable energy and operational flexibility on the technology portfolio and performance of the defossilised petrochemical cluster are not included in the study.

4. Recommendations

Based on the research outputs, limitations and key conclusions of the thesis, the recommendations for future work are:

- Assumptions about hydrogen origin can significantly change the R&D portfolio during the screening and techno-economic assessment of ACS-based technologies. It is because unlike fossil based feedstocks which have zero oxygen content, ACS like CO_2 and biomass has higher oxygen and lower hydrogen content and significant quantities of hydrogen are required for the production of CBB with ACS-based feedstocks. If the hydrogen is considered as an input, the highly CAPEX and energy intensive process of hydrogen production is usually neglected. Therefore, we recommend future studies to always consider the hydrogen origin for technology screening and techno-economic assessment studies of ACS-based CBB production routes.
- ACS like biomass and plastic waste have limited availability and uses in other applications. For example, biomass feedstocks like agriculture residues or waste from wood processing industries are currently used as animal feed, animal bedding, landscaping material and for energy production, respectively. These feedstocks cannot be sourced for CBB production beyond a sustainable limit and further studies should explore these limits. Additionally, to improve the material efficiency of ACS-based processes, it is recommended that further research explores the valorisation of byproducts formed in ACS-based processes considering heavy oil and light gas cracking.
- Defossilising only one product can cause burden shifting in petrochemical clusters, and it is recommended to consider a multi-product approach for defossilising CBB molecules. Further studies should assess potential burden shifts to include the environmental footprint (LCA based) of imports and exports to the cluster.
- The ACS-based processes need around 5 to 10 times more water than the fossil-based counterparts; showing that supporting infrastructures need major changes to accommodate the alternative technologies in the existing cluster. To reduce water stress of the ACS-based processes waste water recycling will be crucial [50,52,53] and further studies should consider wastewater recycling when modelling ACS-based processes.
- It was observed in this study that about 80% to 90% of the CAPEX, equipment footprint and energy needs for the ACS-based processes occurred for the production of naphtha or methanol. Thus, in a resource and space-constrained cluster like the Port of Rotterdam, the import of chemicals like methanol, ethanol, bio-naphtha or pyrolysis oil to synthesise CBB might help to reduce the local demand for resources and space. The impact of these imports on the technology portfolio and their consequences on the performance of the cluster, together with their environmental life cycle assessment, can be further explored.
- Cascading impacts on the minimum selling price of downstream chemicals due to the price increase in the production of CBB using ACS-based processes are uneven for the different value chains and a trickling down effect in prices was observed along them. Further studies could understand this cascading price impacts for specific products to highlight the economic impact for the final consumer.
- In the ACS-based processes, all the hydrocarbon waste streams were incinerated to produce steam, similar to the reference case. This in addition to the endothermic nature of the processes resulted in higher direct CO_2 emissions for the ACS-based processes when compared to the fossil-based counterparts. The direct CO_2 emissions can be further reduced by integrating renewable energy for heat needs and by valorising waste to high-value chemicals. Future study should consider deploying ACS-based technologies in tandem with renewable energy-based utilities for the cluster to be low-carbon.

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Appendix

Appendix A (Chapter 3)

Table A1: CO_2 feedstock based technology ranking for ethylene production

Sl no	Technology	Electricity need (kJ/mol ethylene)	Heat need (kJ/mol ethylene)	Heat production (kJ/mol ethylene)	Carbon utilisation efficiency
Electrochemical based					
1	Direct electrochemical reduction (DER) of CO_2-H_2O to ethylene (C2E)	1332	0	0	100%
2	Direct electrochemical (CO_2 to CO) + Direct electrochemical (CO to Ethylene)	1332	0	0	100%
3	Direct electrochemical (CO_2 to ethanol) + Ethanol dehydration	1332	46	-44	100%
4	Direct electrochemical (CO_2 to methanol) + Methanol to Olefin (MTO)	1413	0	-117	100%
5	Syngas by co-electrolysis-2 + Fischer Tropsch	1429	176	-298	100%
6	Syngas by co-electrolysis-2 + Syngas fermentation + Ethanol Dehydration	1429	264	-386	100%
7	Syngas by co-electrolysis + Water Gas Shift (WGS) + Fischer Tropsch	1458	176	-339	100%
8	CO_2 electrolysis + Water gas shift + Fischer Tropsch	1543	176	-462	33%
9	Direct electrochemical (CO_2 to methane) + Methane autothermal reforming + Fischer Tropsch	1636	0	-370	100%
10	Direct electrochemical (CO_2 to methane) + Methane oxidation to ethane + Ethane oxidation to ethylene	1636	0	-370	100%
11	Direct electrochemical (CO_2 to methane) + Methane aerobic methanotrophs to methanol + Methanol to Olefin (MTO)	1636	0	-370	100%
12	Direct electrochemical (CO_2 to methane) + Methane oxidative coupling to ethylene	1636	0	-370	100%
13	Direct electrochemical (CO_2 to methane) + Methane oxidation to ethane + Ethane cracking to ethylene	1636	136	-506	100%
14	Direct electrochemical (CO_2 to methane) + Methane pyrolysis to acetylene + acetylene hydrogenation	1636	377	-747	100%

15	Direct electrochemical (CO_2 to methane) + Methane dry reforming + Fischer Tropsch	1636	494	-864	50%
16	Direct electrochemical (CO_2 to methane) + Methane steam reforming + Fischer Tropsch	1636	500	-870	100%
17	Syngas by co-electrolysis-1 + Fischer Tropsch	1943	176	-864	50%
Green hydrogen based					
1	Water electrolysis (WE) + CO_2 to methanol (C2M) + Methanol to Olefin (MTO)	1423	0	-304	100%
2	Water electrolysis + CO_2 to ethanol + Ethanol to Olefin (ETO)	1423	46	-349	100%
3	Water electrolysis + Reverse water gas shift + Fischer Tropsch	1423	82	-386	100%
4	Water electrolysis + CO_2 fermentation + Ethanol dehydration	1423	88	-392	100%
5	Water electrolysis + CO_2 to ethane + Ethane cracking	1423	136	-440	100%
6	Indirect electrochemical (Water electrolysis + CO_2 electrolysis + Fischer Tropsch)	1463	0	-298	100%
7	Water electrolysis + CO_2 to ethane + Ethane oxidative cracking	1660	0	-589	100%
8	Water electrolysis + CO_2 to methane (Sabatier) + methane oxidative coupling to ethylene	1897	0	-875	100%
Blue hydrogen based					
1	Steam methane reformer (SMR) + CO_2 to methanol (C2M) + Methanol to olefin (MTO)	0	379	-304	57%
2	Steam methane reformer (SMR) + CO_2 to ethanol + Ethanol to Olefin (ETO)	0	425	-349	57%
3	Steam methane reformer (SMR) + CO_2 fermentation + Ethanol dehydration	0	467	-392	57%
4	Steam methane reformer (SMR) + Reverse water gas shift + Fischer Tropsch	0	461	-386	57%
5	Steam methane reformer (SMR) + CO_2 to ethane + Ethane cracking	0	515	-440	57%

6	Steam methane reformer (SMR) + CO_2 to ethane + Ethane oxidative cracking	0	442	-589	53%
7	Steam methane reformer (SMR) + CO_2 to methane (Sabatier) + methane oxidative coupling to ethylene	0	505	-875	50%
8	Indirect electrochemical (Steam methane reformer (SMR) + CO_2 electrolysis + Fischer Tropsch)	514	253	-298	67%
Hydrogen import based					
1	Hydrogen import (HI) + CO_2 to methane (Sabatier) + methane oxidative coupling to ethylene	0	0	-875	100%
2	Hydrogen import (HI) + CO_2 to ethane + Ethane oxidative cracking	0	0	-589	100%
3	Hydrogen import (HI) + C2M+ Methanol to Olefin (MTO)	0	0	-304	100%
4	Hydrogen import (HI) + CO_2 to ethanol + Ethanol to Olefin (ETO)	0	46	-349	100%
5	Hydrogen import (HI) + CO_2 fermentation + Ethanol dehydration	0	46	-349	100%
6	Hydrogen import (HI) + Reverse water gas shift + Fischer Tropsch	0	82	-386	100%
7	Hydrogen import (HI) + CO_2 to ethane + Ethane cracking	0	136	-440	100%
8	Indirect electrochemical (Hydrogen import (HI) + CO_2 electrolysis + Fischer Tropsch)	514	0	-298	100%

Table A2: Biomass feedstock based technology ranking for ethylene production

Sl no	**Technology**	**Electricity need (kJ/mol ethylene)**	**Heat need (kJ/mol ethylene)**	**Heat production (kJ/mol ethylene)**	**Carbon utilisation efficiency**
Fermentation based					
1	Biomass fermentation to ethanol + Ethanol dehydration	0	88	-98	67%
Anaerobic digestion based					

1	Biogas production + Methane oxidative coupling to ethylene	0	0	-540	50%
2	Biogas production + Methane autothermal reforming + Fischer Tropsch	0	0	-540	50%
3	Biogas production + Biogas aerobic methanotrophs to methanol + Methanol to Olefin (MTO)	0	0	-540	50%
4	Biogas production + Methane steam reforming + Fischer Tropsch	0	500	-1040	50%
5	Biogas production + Methane dry reforming + Fischer Tropsch	0	494	-1034	33%
Steam gasification based					
1	Biomass steam gasification (BSG) + Fischer Tropsch (FT)	0	282	-364	67%
2	Biomass steam gasification + Syngas to Methanol + Methanol to olefin (MTO)	0	282	-364	67%
3	Biomass steam gasification + Syngas fermentation + Ethanol dehydration	0	370	-452	67%
4	Biomass steam gasification + Fischer Tropsch to Ethane + Ethane thermal cracking	0	418	-500	67%
5	Biomass steam gasification + Fischer Tropsch to Ethane + Ethane oxidation cracking	0	349	-928	50%
6	Biomass steam gasification + Syngas to methane + Methane oxidative coupling to ethylene	0	349	-928	50%
7	Biomass pyrolysis to biochar + Biochar steam gasification + Fischer Tropsch	0	701	-1281	50%
8	Biomass steam gasification + Fischer Tropsch to Ethane + Ethane dry cracking	0	526	-1106	40%
Oxygen gasification based					
1	Biomass oxygen gasification (BOG) + Fischer Tropsch (FT)	0	0	-1575	33%
2	Biomass air/O_2 gasification + Syngas to Methanol + Methanol to Olefin (MTO)	0	0	-1575	33%
3	Biomass O_2/air gasification + Syngas fermentation + Ethanol dehydration	0	88	-1663	33%

4	Biomass air/O_2 gasification + Fischer Tropsch to Ethane + Ethane thermal cracking	0	136	-1711	33%
5	Biomass air/O_2 gasification + Fischer Tropsch to Ethane + Ethane oxidation cracking	0	0	-2073	29%
6	Biomass air/O_2 gasification + Fischer Tropsch to Ethane + Ethane dry cracking	0	177	-2250	29%
7	Biomass air/O_2 gasification + Syngas to methane + Methane oxidative coupling to ethylene	0		-2543	25%
Green hydrogen based					
1	Biomass steam gasification (BSG) + Water electrolysis (WE) + Fischer Tropsch (FT)	474	215	-371	100%
2	Biomass oxygen gasification (BOG) + Water electrolysis (WE) + Fischer Tropsch (FT)	949	0	-727	100%
Blue hydrogen based					
1	Biomass steam gasification (BSG) + Steam methane reformer (SMR) + Fischer Tropsch (FT)	0	342	-371	80%
2	Biomass oxygen gasification (BOG) + Steam methane reformer (SMR) + Fischer Tropsch (FT)	0	253	-727	67%
Electrochemical based					
1	Biomass fermentation to ethanol + Ethanol dehydration + Direct electrochemical reduction of CO_2 to ethylene	444	59	-65	100%
2	Biomass steam gasification (BSG) + Water gas shift (WGS) + Fischer Tropsch (FT) + Direct electrochemical reduction of CO_2 to ethylene	444	188	-243	100%
3	Biogas production + Methane oxidative coupling to ethylene + Direct electrochemical reduction of CO_2 to ethylene	444	0	-360	75%
4	Biomass oxygen gasification (BOG) + Water gas shift (WGS) + Fischer Tropsch (FT) + Direct electrochemical reduction of CO_2 to ethylene	444	0	-1050	50%
Hydrogen import based					
1	Biomass oxygen gasification (BOG) + Hydrogen import (HI) + Fischer Tropsch (FT)	0	0	-727	100%

2	Biomass steam gasification (BSG) + Hydrogen import (HI) + Fischer Tropsch (FT)	0	215	-371	100%

Table A3: Plastic feedstock based technology ranking for ethylene production

Sl no	Technology	Electricity need (kJ/mol ethylene)	Heat need (kJ/mol ethylene)	Heat production (kJ/mol ethylene)	Carbon utilisation efficiency
High temperature pyrolysis based					
1	Plastic high temperature pyrolysis (PHTP)	0	106	0	100%
Low temperature pyrolysis based					
1	Plastic low temperature pyrolysis (PLTP) + Pyrolysis oil steam cracking (POSC)	0	402	0	100%
Steam gasification based					
1	Plastic steam gasification (PSG) + Fischer Tropsch (FT)	0	404	-298	100%
2	PE steam gasification + CO to Methanol + Methanol to olefin (MTO)	0	404	-298	100%
3	PE steam gasification + CO to Ethanol + Ethanol dehydration	0	450	-344	100%
4	PE steam gasification + CO to ethane + Ethane thermal cracking	0	540	-434	100%
5	PE steam gasification + CO to ethane + Ethane autothermal cracking	0	505	-725	80%
6	PE steam gasification + CO to ethane + Ethane dry cracking	0	683	-903	80%
7	PE steam gasification + Syngas to methane + Methane oxidative coupling to ethylene	0	606	-1153	67%
Oxygen gasification based					
1	PE O_2 gasification + Water gas shift (WGS) + Fischer Tropsch	0	44	-590	67%
2	Plastic oxygen gasification (POG) + Fischer Tropsch (FT)	0	0	-1199	50%
3	PE O_2 gasification + CO to Methanol + Methanol to olefin (MTO)	0	0	-1199	50%

4	PE O_2 gasification + CO to Ethanol + Ethanol dehydration	0	46	-1245	50%
5	PE O_2 gasification + CO to ethane + Ethane thermal cracking	0	136	-1335	50%
6	PE O_2 gasification + CO to ethane + Ethane autothermal cracking	0	0	-1852	40%
7	PE O_2 gasification + CO to ethane + Ethane dry cracking	0	177	-2029	40%
8	PE O_2 gasification + Syngas to methane + Methane oxidative coupling to ethylene	0	0	-2504	33%
Green hydrogen based					
1	Plastic oxygen gasification (POG) + Water electrolysis (WE) + Fischer Tropsch (FT)	474	0	-466	100%
Blue hydrogen based					
1	Plastic oxygen gasification (POG) + Steam methane reformer (SMR) + Fischer Tropsch (FT)	0	126	-466	80%
Electrochemical based					
1	Plastic oxygen gasification (POG) + Fischer Tropsch (FT) + Direct electrochemical reduction of CO to ethylene	409	0	-317	100%
Hydrogen import based					
1	Plastic oxygen gasification (POG) + Hydrogen import (HI) + Fischer Tropsch (FT)	0	0	-466	100%

Appendix B (Chapter 4 and Chapter 5)

Table B1: CO_2 feedstock composition and values used in the models

Components	Beverage (Grade I) [144–146]	Selected values used in the models (mole fraction)
CO_2 (v/v)	99.9% min	0.999873
Moisture (v/v)	20 ppm max	2e-05
Oxygen (v/v)	30 ppm max	3e-05
Ammonia (v/v)	2.5 ppm max	2.5e-06
NO/NO_2 (v/v)	2.5 ppm max each	2.5e-06 (NO)
N_2 (v/v)	-	-
Non-volatile residue/ particulates (w/w)	10 ppm max	Neglected
Non-volatile organic residue/ oil and grease (w/w)	5 ppm max	
Phosphine (v/v)	0.3 ppm max	3e-07
Total volatile hydrocarbons (calculated as methane) (v/v)	50 ppm max of which 20 ppm max non-methane hydrocarbons	5e-05
Acetaldehyde (v/v)	0.2 ppm max	2e-07
Aromatic hydrocarbon/ Total hydrocarbon (v/v)	0.02 ppm max	2e-08 (Benzene)
CO (v/v)	10 ppm max	1e-05
Methanol (v/v)	10 ppm max	1e-05
HCN (v/v)	0.5 ppm max	5e-07
Halocarbons (v/v)	-	-
Total sulfur (H_2S) (v/v)	0.1 ppm max	1e-07
Total sulfur (as SO_2) excluding SO_2 (v/v)	0.1 ppm max	1.1e-06
SO_2 (v/v)	1 ppm max	
H_2 (v/v)	-	-

Table B2: Biomass feedstock composition (Abbreviation: daf- dry ash free, LHV- lower heating value)

	Composition	Wt%	Wt % dry	Wt % daf
Wood pellets [133,147]	Moisture	8.10%	0.00%	0.00%
	Ash	0.28%	0.30%	0.00%
	Carbon	46.60%	50.71%	50.86%
	Hydrogen	5.61%	6.10%	6.12%
	Nitrogen	0.06%	0.07%	0.07%
	Oxygen	39.34%	42.81%	42.94%
	Sulfur	0.01%	0.01%	0.01%
	Sum	100.00%	100.00%	100.00%
	LHV (MJ/kg daf)	18.72		
	Char fraction (kg char/ kg daf)	0.1752		

Table B3: Plastic waste composition used for the modelling of the plastic pyrolysis process (Abbreviations: PE- polyethylene, LDPE- low density polyethylene, PP- polypropylene, PET- polyethylene terephthalate, PS- Polystyrene, PVC- Polyvinyl chloride, S- Sulfur

DKR (Deutsche Kunststoff Recycling) Standards) [148–150]	Components	Simulation value (mass fraction)
DKR 329	PE (89-90 wt% PE, 10-11 wt% PP and sub-percentage others)	LDPE= 89%, PP= 10%, PVC=0.5%, PET= 0.4%, S= 0.1%
DKR 324	PP (87-88 wt% PP, 8-10 wt% PE and sub-percentage others)	LDPE= 11%, PP= 88%, PVC=0.5%, PET= 0.4%, S= 0.1%

Table B4: Municipal plastic waste composition used for the modelling of the plastic steam gasification process (Abbreviation: daf- dry ash free, ar- as received)

Proximate analysis [151]		
Moisture	10	wt% (ar)
Fixed carbon	0	wt% (daf)
Volatile matter	95.6	wt% (daf)
Ash	4.4	wt% (dry)
Ultimate analysis [151]		
Ash	4.4	wt% (daf)
Carbon	81.11	wt% (daf)
Hydrogen	13.33	wt% (daf)
Nitrogen	0.11	wt% (daf)
Chlorine	0.21	wt% (daf)
Sulfur	0.01	wt% (daf)
Oxygen	0.83	wt% (daf)
Sulfanal [151]		
Pyritic	0.01	wt% (daf)

Table B5: Property method used for the different ethylene production models

Feedstock	Process model	Property method
Naphtha	Naphtha steam cracker	• Global method (cracker): SRK, • ACET-EXT hierarchy: SR-POLAR, • BENZENE hierarchy: NRTL-RK, • SCRUB hierarchy: ENRTL-RK, • SPLITTER hierarchy: RKS-BM, • Butadiene extraction hierarchy: NRTL-RK, • O1-E22/O1-D3/O1-D4/SCRUB-SP hierarchy: UNIQUAC-RK.
CO_2	CO_2 direct electrochemical reduction to ethylene	• Global property method- ENRTL-RK, • SEP hierarchy: RKS-BM.
	Water electrolysis + CO_2 hydrogenation to methanol + methanol to olefin	• Global property method (water electrolysis): ENRTL-RK. • Global property method (CO_2 to methanol): RK-SOAVE. • Global property method (MTO): RK-SOAVE, • SEP: RKS-BM

Biomass	Water electrolysis + Biomass steam gasification + CO_2 hydrogenation to methanol + syngas Fischer Tropsch + methanol to olefin	• Global property method (water electrolysis): ENRTL-RK. • Global property method (biomass): NRTL-RK, • C2SEP: SR-POLAR, • DISTIL: RK-SOAVE, • Gasifier: NRTL-RK, • MTO: RK-SOAVE, • SEP: RKS-BM, • TARSEP: UNIFAC.
	Water electrolysis + Biomass steam gasification + CO or CO_2 hydrogenation to methanol + methanol to olefin	• Global property method (water electrolysis): ENRTL-RK. • Global property method (biomass to methanol): NRTL-RK, • CO-MTL: RK-SOAVE, • CO_2-MTL: RK-SOAVE, • DISTIL: RK-SOAVE, • Gasifier: NRTL-RK, • TARSEP: UNIFAC. • Global property method (MTO): RK-SOAVE, • SEP: RKS-BM
Plastic	Plastic low temperature pyrolysis + pyrolysis oil steam cracking	• Global property method (water electrolysis): ENRTL-RK. • Global property method (pyrolysis): POLYSRK. • Global method (cracker): SRK, • ACET-EXT hierarchy: SR-POLAR, • BENZENE hierarchy: NRTL-RK, • SCRUB hierarchy: ENRTL-RK, • SPLITTER hierarchy: RKS-BM, • Butadiene extraction hierarchy: NRTL-RK, • O1-E22/O1-D3/O1-D4/SCRUB-SP hierarchy: UNIQUAC-RK.
	Plastic steam gasification + syngas hydrogenation to methanol + methanol to olefin	• Global property method: PR-BM, • Methanol Hierarchy: RK-SOAVE. • Global property method (MTO): RK-SOAVE, • SEP: RKS-BM

Table B6: Property method used for the different feedstock-based benzene production models.(Abbreviations: MTL: Methanol, MTA: Methanol to aromatics, TBD: Toluene to benzene, BTX: Benzene, toluene, xylene, NTRL: Non-random two liquid, RK: Redlich Kwong, SRK: Soave Redlich Kwong, UNIQUAC: Universal quasi chemical, UNIF-LL: Universal functional activity coefficient for liquid-liquid, ENRTL: Electrolyte non-random two liquid, RKS: Redlich Kwong Soave, BM: Boston Mathias alpha function, PR: Peng Robinson)

Feedstock	Process model	Property method
Pygas, reformate and C7+	Aromatics processing plant	• Global method (Aromatics): NRTL-RK, • H_2 recovery: SRK • Extraction and solvent recovery: UNIQUAC • Decanter: UNIF-LL
CO_2	Water electrolysis + CO_2 hydrogenation to methanol +	• Global property method (water electrolysis): ENRTL-RK.

	methanol to aromatics + Toluene disproportionation to benzene + Xylene isomerisation (WE+ C2M+ MTA + TDB + XI)	• Global property method (CO_2 to methanol): RK-SOAVE. • Global property method (MTA): ENRTL-RK, • MTA reactor: RK-SOAVE • SPLITTER: RKS-BM • TDB: SRK • BTX: ENRTL-RK
Biomass	Water electrolysis + Biomass steam gasification + CO or CO_2 hydrogenation to methanol + methanol to aromatics + Toluene disproportionation to benzene + Xylene isomerisation (BSG + S2M and WE+C2M + MTA + TDB + XI)	• Global property method (water electrolysis): ENRTL-RK. • Global property method (biomass to methanol): NRTL-RK, • CO-MTL: RK-SOAVE, • CO_2-MTL: RK-SOAVE, • DISTIL: RK-SOAVE, • Gasifier: NRTL-RK, • TARSEP: UNIFAC. • Global property method (MTA): ENRTL-RK, • MTA reactor: RK-SOAVE • SPLITTER: RKS-BM • TDB: SRK • BTX: ENRTL-RK
Plastic	Plastic steam gasification + syngas hydrogenation to methanol + methanol to aromatics + Toluene disproportionation to benzene + Xylene isomerisation (PSG+ S2M+ MTA + TDB + XI)	• Global property method: PR-BM, • Methanol Hierarchy: RK-SOAVE. • Global property method (MTA): ENRTL-RK, • MTA reactor: RK-SOAVE • SPLITTER: RKS-BM • TDB: SRK • BTX: ENRTL-RK

Table B7: CAPEX and fixed OPEX calculation assumptions (Abbreviations: ISBL- Inside battery limit, OSBL- Outside battery limit)

CAPEX [100]		**Fixed OPEX** [100]	
ISBL cost	3.3*Bare equipment cost	Maintenance cost	3%*ISBL
OSBL cost	40%*ISBL	Capital charges and royalties	4%*(ISBL+ OSBL+EN)
Engineering costs (EN)	10%* (ISBL+OSBL)	Labour, supervision and overhead cost	1.875*Labour estimates
Contingency (CN)	10%* (ISBL+OSBL)	Corporate income tax	25%*Operating income
Working capital	5%*(ISBL+OSBL+ EN+ CN)	Land and building rents, insurance, property taxes and environmental charges	5%*(ISBL+ OSBL)

Appendix C (Chapter 6)

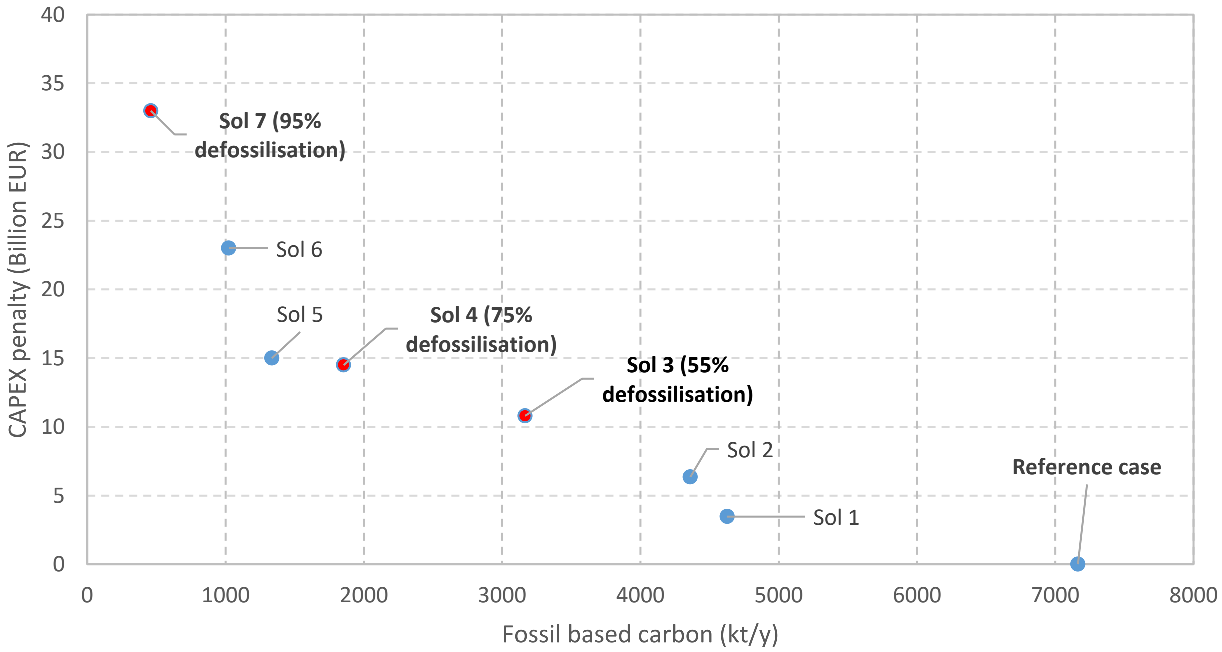

Figure C1: Pareto front for Case 2

Note: In Figure C1, the solutions that obtained 55% (sol 3), 75% (sol 4), and 95% (sol 7) defossilisation in Case 2 are highlighted and these are the ones considered for discussion. The Pareto front is discontinuous because only the solutions corresponding to processes with an operational margin of 10% or less are represented.

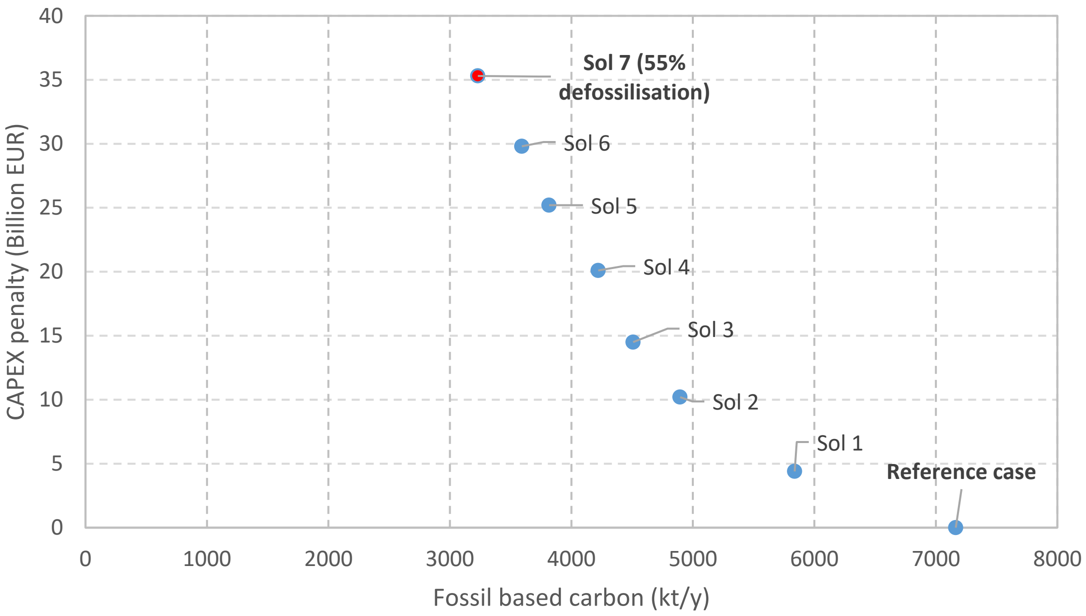

Figure C2: Pareto front for Case 3

Note: In Figure C2, the solution that obtained 55% (sol 7) defossilisation in Case 3 is shown and it is the one considered for discussion. There are no 75% and 95% defossilisation solutions in Case 3, due to the ACS limits. The Pareto front is discontinuous because only the solutions corresponding to processes with an operational margin of 10% or less are represented.

Appendix D (All the description in this appendix as well as figures and equations are taken from Tan et al[138]) (Chapter 6)

Definition of the layers and nodes

To develop the model, a graph representation was used to set up the superstructure-based optimisation model. In this representation, the nodes represent the available feedstocks, desired products, chemical processes, utility generation processes, energy sinks, and energy sources. The links in the graph illustrate potential interconnections between the different nodes. To distinguish between material and energy interconnections, the model used separate layers for material and energy flows. This approach allowed separate constraints to be enforced in each respective layer. A generic representation of the superstructure used is shown in Figure D1, where the top part of the figure shows the material layer and the bottom is the energy layer.

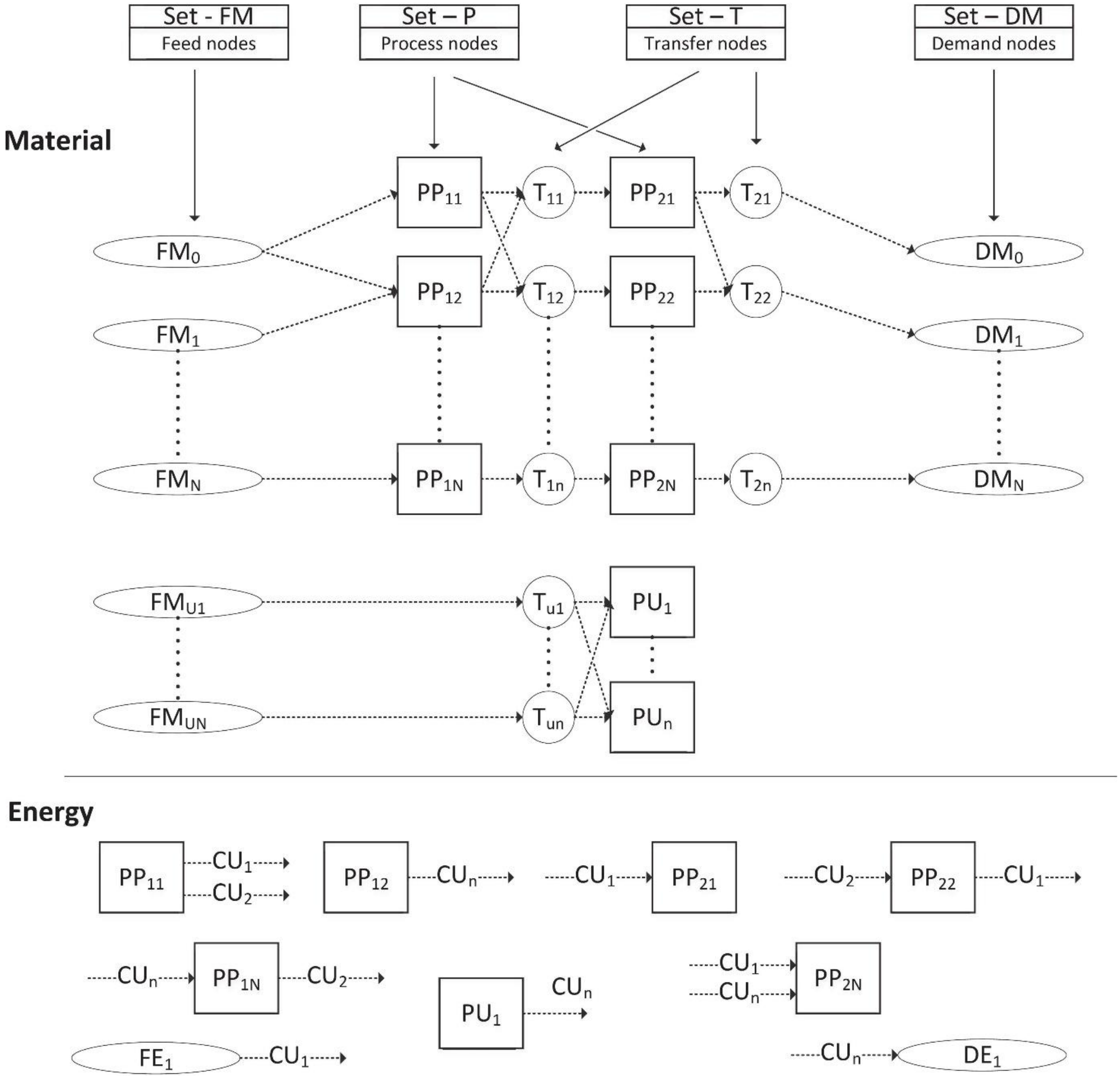

Figure D1: Generic superstructure representation. In the figure, FM_n is a material feed node, FE_n is an energy feed node, PP_n is a chemical process node, PU_n is a utility process, T_n is a transfer node, DM_n is a material demand node, and DE_n is an energy demand node.

The connections in the material layer are explicitly defined to match the pre-existing value chains in a petrochemical cluster. In the model, transfer nodes were defined to distribute the required chemical materials to the different process nodes and demand nodes. The model will select the optimal processing routes and optimal starting feedstocks to produce the required chemical products. In addition to the fossil-based processes from the existing value chains, the model also contains ACS-based processes, which can be disabled in the model to make them unavailable as a potential solution. For modelling the energy layer, the energy equations are solved based on the proximity of nodes to each other using an approach that matches the energy demand and energy supply. In contrast to the material layer, the links are not explicitly defined using transfer nodes. This approach allows all potential connections between nodes to be considered when closing the energy balance.

All nodes in the system belong to a set ***B***. The *transfer nodes* were grouped together (subset ***T***⊂***B***). The process and utility generation nodes were grouped together as *process nodes* (subset ***P***⊂***B*)**. The *process nodes* were further divided into *chemical processes* (subset ***PP***⊂***P***), and *utility generation processes* (subset ***PU***⊂***P***). The chemical processes were further subdivided into *fossil-based chemical processes* (subset $\boldsymbol{PP}_{Fossil}$⊂***PP***) and *ACS-based chemical processes* (subset $\boldsymbol{PP}_{ACS}$⊂***PP***). The subset of utility generation processes was further subdivided into *fossil-based utility generation processes that could generate heat and or electricity* (subset $\boldsymbol{PU}_{Fossil}$⊂***PU***) and *electricity only based utility generation processes* (subset $\boldsymbol{PU}_{Electric}$⊂***PU***). All the different process subsets convert material and/or utilities into other materials and/or utilities.

The product nodes and energy sink nodes were grouped together as *demand nodes* (subset ***D***⊂***B***). These demand nodes were divided into *material demand nodes* (subset ***DM***⊂***D***) and *energy demand nodes* (subset ***DE***⊂***D***). The demand for the end-of-value chain chemicals was enforced at the material demand nodes (i.e., the system should produce the chemicals demanded by the outside system) and they act as overflow nodes for other potential products. The energy sink nodes represent the export of excess energy to the outside system.

Similar to the material demand nodes, the material feed and energy source nodes were grouped together as *feed nodes* (subset ***F***⊂***B***), and divided into *material feed nodes* (subset ***FM***⊂***F***) and *energy source nodes* (subset ***FE***⊂***F***). The material feed nodes act as the carbon sources for the chemical processes, while the energy source nodes represent the import of energy into the system.

Additionally, chemical and utility components were defined in the model. For the material layer, chemical components ***CC*** (e.g., methyl *tert*-butyl ether, ethylene, propylene) were defined, while utilities ***CU*** (e. g., low-pressure steam, electricity, refrigerants) were defined for the energy layer.

Petrochemical clusters can consist of multiple cluster sites with one to several companies present per cluster site. Examples of such subclusters are, for instance, a chlorine cluster, an ethylene cluster, etc. These cluster sites can be physically separated by a significant distance, making it difficult to transport some energy flows (e.g., low-pressure steam) between cluster sites. To take this into account, in the model, energy streams are constrained to the nodes within a given subcluster site, while material streams can cross the subcluster site boundaries. For the subcluster sites, a new set ***CS*** was defined. Where the nodes present on a cluster site were grouped together as (subset $\boldsymbol{B}_{CS}$⊂***B***).

Material equations

In Figure D2, the standard data structure for the nodes and the process nodes is presented. Each node *b* in the material layer has a total material mass flow of component *cc* ($Mass_{b,cc}^{In}$). This is estimated as a mass balance, i.e., it is calculated based on all material streams flowing into the node. Similarly, each node has a total material mass flow of component *cc* leaving the node ($Mass_{b,cc}^{Out}$). The total mass flow going into a node is calculated using Eq. (1). Where, $Streams_{i,b,cc}^{Mass}$ is the mass flow rate of component *cc* going from node *i* to node *b*. For material feed nodes, the mass flowrate into the nodes is calculated using Eq. (2), where $Feed_{f}^{Mass}$ is the mass flow rate of the available feedstock, $X_{f,cc}^{FeedComp}$ is the composition of the feedstock, f_f^I is the feed node integer indicating whether a feed node is present (a value of zero indicates the feed node is inactive while a value of one indicates is active).

$$Mass_{b,cc}^{In} = \sum_{i \in \mathbf{B}, i \neq b} Streams_{i,b,cc}^{Mass} \quad \forall b \in \mathbf{B} \wedge b \notin \mathbf{F}, \forall cc \in \mathbf{CC} \tag{1}$$

$$Mass_{f,cc}^{In} = Feed_f^{Mass} \cdot X_{f,cc}^{FeedComp} \cdot f_f^i \quad \forall f \in \mathbf{FM}, \forall cc \in \mathbf{CC} \tag{2}$$

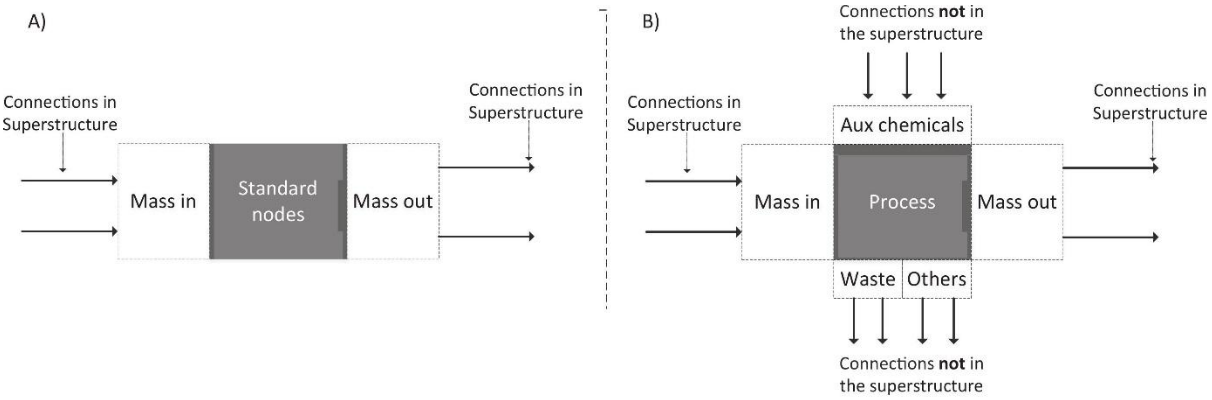

Figure D2: Schematic of the data structure for the nodes (except process nodes) and for the process nodes.

The mass flow rate out from a process node is based on the conversion of material in the node. This mass of transformed material is assumed to scale linearly based on the mass flow into the node. For each node, a limiting component cc^* was selected that scales linearly with the inputs and outputs of the process node. For instance, for the production of ethylene oxide, ethylene was selected as the limiting component. Besides the limiting component, processes also may have a demand for additional chemicals that are provided by other processes that are part of the superstructure. This demand is enforced by using Eq. (3), where $Mass_{p,cc*}^{In}$ is the mass flow rate of the limiting component going into process node p and $X_{p,cc}^{Mass,In}$is the material demand parameter of the process node. Other material demands that are not produced by processes within the superstructure, such as solvents, are determined using Eq. (4), where $X_{p,cc}^{Mass,In,Aux}$ is the auxiliary demand parameter.

$$Mass_{p,cc}^{In} = Mass_{p,cc*}^{In} \cdot X_{p,cc}^{Mass,In} \quad \forall p \in \mathbf{P}, \forall cc \in \mathbf{CC} \tag{3}$$

$$Mass_{p,cc}^{In,Aux} = Mass_{p,cc*}^{In} \cdot X_{p,aux\_sp,cc}^{Mass,In,Aux} \quad \forall p \in \mathbf{P}, \forall cc \in \mathbf{CC} \tag{4}$$

Therefore, the mass out of a process node p is given by Eq. (5), where $X_{p,cc}^{P}$ is the conversion parameter of the process node. In addition to the main products, every process produces several streams of by-products and waste materials that are not shared with other nodes and are, therefore, not part of the connections in the superstructure. The mass flow rate of a by-product stream sp is calculated using Eq. (6) and the mass flow rate of waste stream sw is determined using Eq. (7).

$$Mass_{p,cc}^{Out} = Mass_{p,cc*}^{In} \cdot X_{p,cc}^{P} \quad \forall p \in \mathbf{P}, \forall cc \in \mathbf{CC} \tag{5}$$

$$Mass_{p,sp,cc}^{Out,Side} = Mass_{p,cc*}^{In} \cdot X_{p,sp,cc}^{P,Side} \quad \forall p \in \mathbf{P}, \forall cc \in \mathbf{CC} \tag{6}$$

$$Mass_{p,sw,cc}^{Out,Waste} = Mass_{p,cc*}^{In} \cdot X_{p,sw,cc}^{P,Waste} \quad \forall p \in \mathbf{P}, \forall cc \in \mathbf{CC} \tag{7}$$

The mass out of demand node d is given by Eq. (8), where d_d^i is the demand node integer indicating whether the demand node is present (the demand node is absent with a value of zero and present with a value of one). For other types of nodes in the model, such as transfer nodes, there is no conversion of material, therefore, the material flow into a node is equal to the material flow out of the node as given in Eq. (9).

$$Mass_{d,cc}^{Out} \cdot d_d^i = Mass_{d,cc}^{In} \quad \forall d \in \mathbf{DM}, \forall cc \in \mathbf{CC} \tag{8}$$

$$Mass_{b,cc}^{Out} = Mass_{b,cc}^{In} \quad \forall b \in \mathbf{B} \wedge b \notin \mathbf{D} \wedge b \notin \mathbf{P}, \forall cc \in \mathbf{CC} \tag{9}$$

As pointed out before, the purpose of the transfer nodes is to distribute chemicals among the material demand nodes and the processes requiring those chemicals. The mass flow rate of a component subset cc between transfer node subset t and node subset j is calculated using Eq. (10), where $y_{t,j}$ is the transfer coefficient. To make sure that the total mass flow rate of the links leaving the transfer node does not exceed mass out of the transfer node, an additional constraint is introduced (Eq. (11)). For the other nodes, the mass flow of a component cc in a link going from node b to node j is calculated using Eq. (12). In this equation, a separation factor $S_{b,j,cc}$ is used to distribute the fraction of each component in $Mass_{b,cc}^{Out}$ to the outgoing links going from node b to node j.

$$Streams_{t,j,cc}^{Mass} = Mass_{t,cc}^{Out} \cdot y_{t,j} \quad \forall j \in \mathbf{B}, \forall t \in \mathbf{T}, \forall cc \in \mathbf{CC} \tag{10}$$

$$\sum_{j \in \mathbf{B}, j \neq t} y_{t,j} = 1 \quad \forall t \in \mathbf{T} \tag{11}$$

$$Streams_{b,j,cc}^{Mass} = Mass_{b,cc}^{Out} \cdot S_{b,j,cc} \quad \forall b \in \mathbf{B} \wedge b \notin \mathbf{T}, \forall j \in \mathbf{B}, \forall cc \in \mathbf{CC} \tag{12}$$

Furthermore, each chemical process node was assumed to have an operating window. The lower and upper boundary of the production capacity was set using Eq. (13)for the fossil chemical processes and Eq. (14) for the ACS-based processes. Where, $K_{p,fossil}^{Flex}$ is a capacity flexibility parameter of the fossil processes and $K_{p,ACS}^{Flex}$ is the capacity flexibility parameter of the ACS-based processes. These capacity flexibility parameters are defined as the fraction that the process can deviate from its nominal production capacity. For instance, with a value 0.1, a process can downscale its production by 10 %. p_p^I is the positive process integer value, where if a process is not present, a value of zero is given, and where any positive integer indicates the number of times that a process is present in the cluster (for instance, three plants producing methanol). $K_{p,cc}^{Cap}$ is the nominal production capacity of component cc of process p. The bounds of the process decision variable are set using Eq. (15), where $p_p^{I,LB}$ and $p_p^{I,UB}$ are the lower and upper bounds of p_p^I, respectively.

$$\left(1 - K_{p,fossil}^{Flex}\right) p_p^I \cdot K_{p,cc}^{Cap} \leq Mass_{p,CC}^{Out} \leq p_p^I \cdot K_{p,cc}^{Cap} \quad \forall p \in \mathbf{PP}_{Fossil}, \forall cc \in \mathbf{CC} \tag{13}$$

$$\left(1 - K_{p,ACS}^{Flex}\right) p_p^I \cdot K_{p,cc}^{Cap} \leq Mass_{p,CC}^{Out} \leq p_p^I \cdot K_{p,cc}^{Cap} \quad \forall p \in \mathbf{PP}_{ACS}, \forall cc \in \mathbf{CC} \tag{14}$$

$$p_p^{I,LB} \leq p_p^I \leq p_p^{I,UB} \quad \forall p \in \mathbf{P} \tag{15}$$

Finally, a chemical production demand is enforced on the material demand nodes of chemicals at the end of each value chain using Eq. (16). This chemical production demand is the export demand for the end-of- value chemicals (e.g., MTBE and styrene monomer) in the model.

In Eq. (16), K_d^{Tol} is the tolerance parameter of the lower boundary and $X_{f,cc}^{Demand}$ is the existing production rate of chemical *cc*. In the current version, the model is allowed to exceed the base export demand by 20 %. However, it is possible to run the model with lower or higher percentages.

$$\left(1-K_d^{Tol}\right) \le \frac{Mass_{d,CC}^{Out}}{X_{d,cc}^{Demand}} \le 1.2 \quad \forall d \in \mathbf{D}, \forall cc \in \mathbf{CC} \tag{16}$$

Energy equations

In the energy layer, all chemical process and utility generation nodes have an energy demand and supply. The energy demand $Energy_{p,cu}^{Demand}$ for utility *cu* is calculated based on the mass flow rate going into the node of the limiting component $Mass_{p,cc*}^{In}$ in the material layer and is given by Eq. (17). In this equation, $X_{p,cu}^{Demand}$ is a utility demand parameter relating the demand for a utility *cu* to $Mass_{p,cc*}^{In}$.

$$Energy_{p,cu}^{Supply} = Mass_{p,cc*}^{In} \cdot X_{p,cu}^{Supply} \quad \forall p \in \mathbf{P}, \forall cu \in \mathbf{CU} \tag{17}$$

The energy supply of the chemical process utility generation nodes is based on the mass flowrate of the limiting component and is given in Eq. (18), where $X_{p,cu}^{Supply}$ is a utility supply parameter.

$$Energy_{p,cu}^{Demand} = Mass_{p,cc*}^{In} \cdot X_{p,cu}^{Demand} \quad \forall p \in \mathbf{P}, \forall cu \in \mathbf{CU} \tag{18}$$

In addition to the chemical process and utility generation nodes in the model, each cluster site has an energy source node and an energy sink node. The energy sink node acts as the outgoing energy connection which exports excess energy outside the system boundaries of the cluster, while the energy source node acts as the incoming energy connection for importing energy into the cluster. To ensure that, for a given cluster site *cs,* the model does not simultaneously import and export the same utility flow, an additional binary variable p_{cs}^{i} was introduced. The energy supply for the energy source and energy demand for the energy sink nodes were determined using Eqs. (19) and (20).

$$Energy_{f,cu}^{Supply} = f_{f,cu} p_{cs}^{I} \quad \forall f \in \mathbf{FE}, \forall cu \in \mathbf{CU} \tag{19}$$

$$Energy_{d,cu}^{Demand} = d_{d,cu}\left(1-p_{cs}^{I}\right) \quad \forall d \in \mathbf{DE}, \forall cu \in \mathbf{CU} \tag{20}$$

Based on the energy supply and energy demand of nodes in a cluster site, the total site energy demand and supply of a utility *cu* was calculated using Eqs. (21) and (22).

$$Energy_{cs,cu}^{Total,Supply} = \sum_{i \in \mathbf{B_{CS}}} Energy_{i,cu}^{Supply} \quad \forall cs \in \mathbf{CS}, \forall cu \in \mathbf{CU} \tag{21}$$

$$Energy_{cs,cu}^{Total,Demand} = \sum_{i \in \mathbf{B_{CS}}} Energy_{i,cu}^{Demand} \quad \forall cs \in \mathbf{CS}, \forall cu \in \mathbf{CU} \tag{22}$$

For each cluster site, the total energy balance of utility *cu* is closed using Eq. (23), thereby making sure that the total energy demand matches the supply within a cluster site cs_n.

$$Energy_{cs,cu}^{Total,Supply} = Energy_{cs,cu}^{Total,Demand} \quad \forall cs \in \mathbf{CS}, \forall cu \in \mathbf{CU} \tag{23}$$

Like the mass of materials between the model nodes, we would like to track the flow energy between nodes. Therefore, a variable $Streams_{i,b,cu}^{Energy}$ was added that represents the flow of energy from a node *i* to a node *b* for utility *cu*. This variable is determined using Eq. (24), which is an energy balance over node b, ensuring that the inflow and outflow are in balance. Next, a constraint was added that enforces that the total flow of energy of utility *cu* leaving node *b* does not exceed the node's total energy supply of utility *cu*.

This constraint is set using Eq. (25).

$$Energy_{b,cu}^{Supply} + \sum_{j \in \mathbf{B_{CS}}} Streams_{j,b,cu}^{Energy} = Energy_{b,cu}^{Demand} + \sum_{j \in \mathbf{B_{CS}}} Streams_{b,j,cu}^{Energy} \quad \forall cs \in \mathbf{CS}, \forall cu \in \mathbf{CU}, \forall b \in \mathbf{B_{CS}} \tag{24}$$

$$\sum_{j \in \mathbf{B}, j \neq b} Streams_{b,j,cu}^{Energy} \leq Energy_{b,cu}^{Supply} \quad \forall b \in \mathbf{B}, \forall cu \in \mathbf{CU} \tag{25}$$

Following the approach used for the chemical process nodes, each utility generation process was assumed to have an operating window. This operating window was enforced on the utility generation nodes using Eq. (26).

$$\left(1 - K_p^{Flex}\right) p_p^I \cdot K_{p,cu}^{Cap} \leq Energy_{p,cu}^{Suply} \leq p_p^i \cdot K_{p,cu}^{Cap} \quad \forall p \in \mathbf{PU}_{Fossil}, \forall\, cu \in \mathbf{CU} \tag{26}$$

Objective functions

The model described in the previous section allows the evaluation of several objective functions, such as environmental and economic performance indicators. To illustrate this, we examine two objective functions, but similar equations can be formulated for other indicators. As the main goal of the model is to investigate the transformation of petrochemical clusters to the use of alternative carbon sources, the first objective function corresponds to the minimisation of fossil-based carbon sources. This minimisation is given in Eq. (27), where m_f^{Carbon} is the mass fraction of carbon in the fossil-based carbon feedstock *f*.

$$\min \sum_{f \in \mathbf{FM}_{FC}} Feed_f^{Mass}\, m_f^{Carbon} \tag{27}$$

To illustrate the possibilities of the model, the second objective was to minimise the amount of new investments in the cluster while minimising changes to the cluster. The two objective functions imply that in this case, the model will aim to identify configurations that use ACS while minimising stranded assets. The second objective function is given by Eq. (28), in which stranded assets are minimised by including a penalty term. This objective function does not minimise costs, it minimises what we call a "capex penalty", that is, the economic loss associated with stopping the use of current assets plus the new investment required by the new technologies. In the equation, the first term represents the penalty for removing an existing fossil-based process from the cluster. The second term represents the penalty for removing an existing fossil-based utility process, and the third term represents the costs involved in deploying a new ACS-based process in the cluster. In this equation, *CAPEX_p* is the total capital expenditure required for the construction of a process *p*.

$$\min \left(\sum_{p \in \mathbf{PP}_{Fossil}} \left(1 - p_p^I\right) CAPEX_p + \sum_{p \in \mathbf{PU}_{Fossil}} \left(1 - p_p^I\right) CAPEX_p + \sum_{p \in \mathbf{PP}_{ACS}} p_p^I \cdot CAPEX_p + \sum_{p \in \mathbf{BB}_{ACS}} p_p^I \cdot CAPEX_p \right) \tag{28}$$

Using the two objective functions, a Pareto front is generated. It shows the trade-offs between the different solutions of the multi-objective model. There are several ways to construct Pareto fronts, with the ε-constraint method being one of the most well-known methods. In the ε-constraint method, the model is optimised for a single objective function, while the other objective functions are implemented as additional constraints. In this work, the augmented ε-constraint method AUGMECON2 was used to generate the Pareto fronts.

Evaluation of the solutions

In the model, the solutions of the Pareto front are ranked using the Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) method. This method ranks the solutions based on their distance from the ideal and the non-ideal solution between 0 and 1, with the best solution being the closest to 1. The ideal and non-ideal solutions are a combination of the best and worst values of the considered criterion, respectively.

To apply TOPSIS, the desired decision criteria and their associated weights must be defined. Besides the key performance indicators used as objective functions for the creation of the Pareto front, other or alternative KPIs can also be introduced as assessment criteria. In this work, the objective functions used to create the Pareto front were also used to rank the solutions in TOPSIS. The weights allow a decision criteria to be preferred over the others, e.g., prioritising defossilising feedstocks over the associated costs. This approach allows to prioritise the solutions that are closer to the best value associated with that decision criteria.

Two different strategies for solving the model were implemented, with both methods following identical procedures. In the multi-step method, ACS-based processes were added to the solution space over several steps, thereby increasing the number of potential solutions with each step. In the single step method, all potential ACS-based processes are introduced in the model in one single step, thereby allowing the global best solution to be identified as if all options were available at the same time. The multi-step method can be used to identify pathways to reach the configuration of the selected global solution. It allows to identify potential lock-ins introduced by the order in which technologies are deployed. For the model to consider changes that have occurred in a prior step, the following assumptions were made:

- The model has no perfect foresight. It does not know what processes are available in future steps and therefore, only evaluates the potential solutions based on the technologies available on the current step.
- Removed fossil-based processes cannot return in later steps.
- ACS-based processes that are introduced in a step cannot be removed later. This is done to avoid that the model will deploy a plant to just remove it a couple of years later.

In the appendices, Figure D3 shows the flowchart developed for solving the model in a multi-step, multi-objective optimisation manner. First, the baseline fossil-based petrochemical cluster needs to be loaded as a starting point for the model. In each time step of the model, ACS- based processes are added to the solution space of the model. This is done by unlocking the process integer variable value associated with the ACS-based model from a value fixed to “0″ and allowing the variable to be evaluated as part of the optimisation. Next, a Pareto front for the time step is generated using the augmented ε-constraint method (AUGMECON2). Each solution in this Pareto front is ranked using the TOPSIS method. One could allow a decision maker to decide on the best solution among the top-ranked solutions of the Pareto front using an interactive modelling approach. However, in the current implementation, the solution ranked highest by TOPSIS is selected by the model as the best solution.

This best solution is then loaded into the model, allowing all variable values associated with this cluster configuration to be accessed.

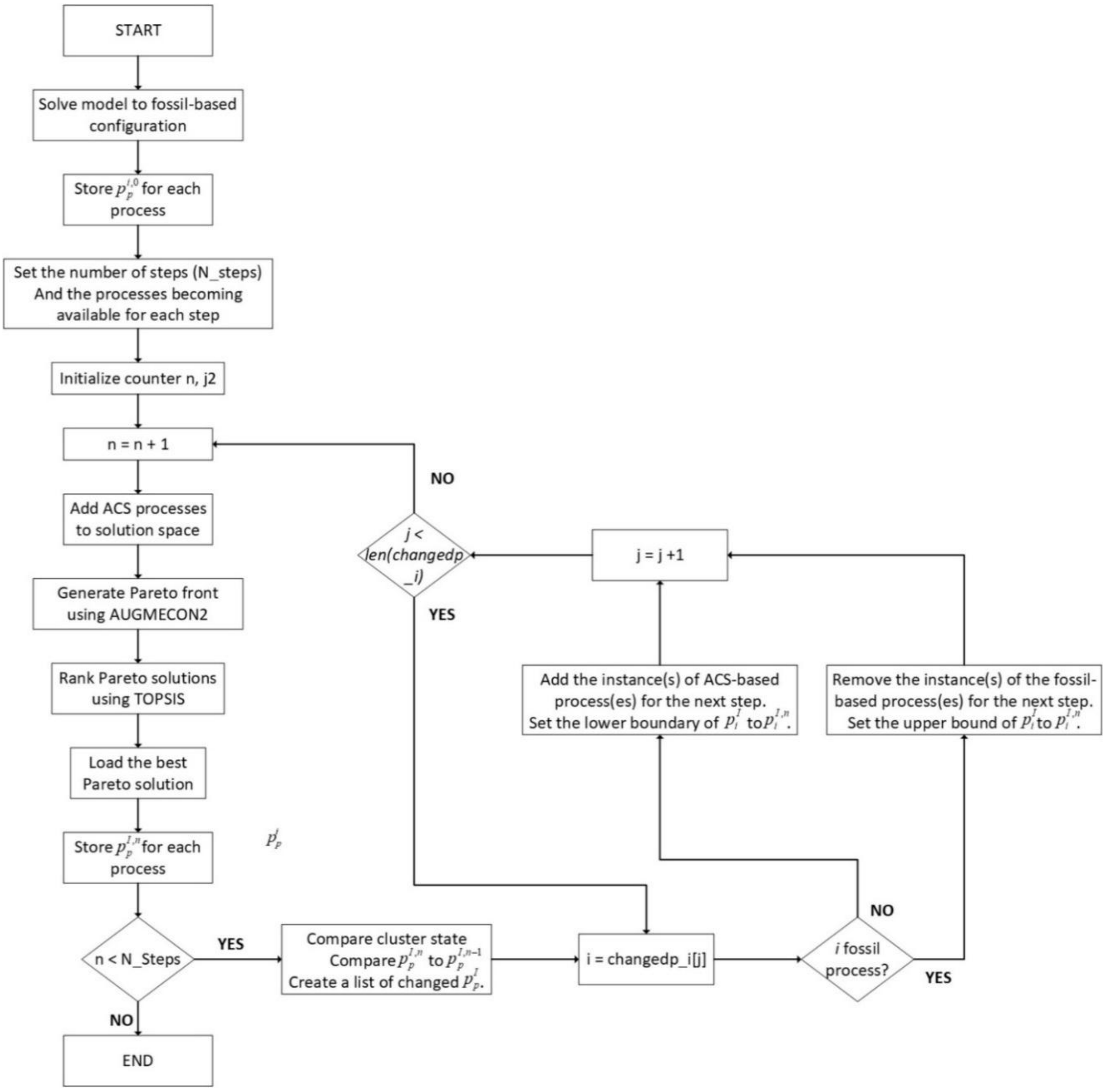

Figure D3: Flowchart for the multi-step multi-objective method

Supplementary Information

The Supplementary Information (SI) includes block flow diagrams, mass balances, energy balances, CAPEX data and Pareto fronts for each case assessed in the study. The chapter specific supplementary information are provided in the 4TU Research Data repository: https://doi.org/10.4121/a057065c-a9a8-46c4-8255-3ee687ed164e

Process model descriptions of fossil-based and ACS-based processes, containing modelling assumptions, mass balances, energy balances, economic data and bibliographic sources are provided in Zenodo:

- Aromatics distillation: https://doi.org/10.5281/zenodo.14894694
- Biomass steam gasification followed by Fischer-Tropsch and methanol-to-olefin: https://doi.org/10.5281/zenodo.14893888
- Biomass steam gasification followed by syngas-to-methanol: https://doi.org/10.5281/zenodo.14894260

- CO_2 hydrogenation to methanol: https://doi.org/10.5281/zenodo.14894463
- CO_2-H_2O Direct electrochemical reduction to ethylene: https://doi.org/10.5281/zenodo.14894342
- Methanol-to-aromatics conversion: https://doi.org/10.5281/zenodo.14894482
- Methanol-to-olefin conversion: https://doi.org/10.5281/zenodo.14894523
- Naphtha steam cracker: https://doi.org/10.5281/zenodo.14825234
- Plastic waste pyrolysis followed by naphtha steam cracking: https://doi.org/10.5281/zenodo.14894590
- Plastic waste steam gasification followed by syngas-to-methanol: https://doi.org/10.5281/zenodo.14894543

The source code of the superstructure-based optimisation can be found in Tan et al's work[99,138].

List of Publications and Conference Appearances

Publications

1. Manalal, J. T.; Pérez-Fortes, M.; Gonzalez, P. I.; Ramirez, A. Evaluation of Alternative Carbon Based Ethylene Production in a Petrochemical Cluster: Technology Screening & Value Chain Impact Assessment. In *Computer Aided Chemical Engineering*; Elsevier Masson SAS, 2023; Vol. 52, pp 2453–2458. https://doi.org/10.1016/B978-0-443-15274-0.50390-5.
2. Manalal, J. T.; Pérez-Fortes, M.; Ramírez, A. Techno-Economic Impacts of Using Alternative Carbon-Based Feedstocks for the Production of Methanol. In *Computer Aided Chemical Engineering*; Elsevier Masson SAS, 2024; Vol. 53, pp 847–852. https://doi.org/10.1016/B978-0-443-28824-1.50142-3.
3. Manalal, J. T., Pérez-Fortes, M., & Ramírez, A. (2025). Re-wiring petrochemical clusters: impact of using alternative carbon sources for ethylene production. Green Chemistry, 27(22), 6641–6659. https://doi.org/10.1039/D4GC06042C
4. Manalal, J. T.; Pérez-Fortes, M.; Ramirez, A. Ripple effects of defossilising aromatics production in petrochemical clusters, 2026 (submitted)
5. Manalal, J. T.; Tan, M.; Pérez-Fortes, M.; Ramirez, A. The impact of feedstock availability on defossilising the production of chemical building blocks, 2026 (submitted)

Conference appearances

1. 2023, June 18th – 21st, 33rd European Symposium on Computer-Aided Process Engineering (ESCAPE 33), Athens, Greece. Evaluation of Alternative Carbon Based Ethylene Production in a Petrochemical Cluster: Technology Screening & Value Chain Impact Assessment. (Oral presentation)
2. 2024, June 2nd – 6th, 34th European Symposium on Computer-Aided Process Engineering (ESCAPE 34)/ 15th International Symposium on Process Systems Engineering (PSE 24), Florence, Italy. Techno-Economic Impacts of Using Alternative Carbon-Based Feedstocks for the Production of Methanol. (Oral presentation)
3. 2024, May 21st, Electrochemical Conversion National Symposium (ECCNS 2024), Den Haag, The Netherlands. The relevance of hydrogen origin for the selection of alternative carbon based technologies: A case study of ethylene production pathways. (Oral presentation)
4. 2024, November 5th, TU Delft Research & Innovation event: Hydrogen & Green Chemistry, Delft, The Netherlands. Why hydrogen origin matters for the screening of alternative carbon-based technologies. (Poster presentation)

Curriculum Vitae

Tonny Manalal was born on 9th March 1992 in Fujairah, United Arab Emirates. In 2014, he obtained his bachelor's degree in Chemical Engineering from Kerala University, India. He worked in BPCL Kochi refinery and Reliance Jamnagar refinery in India for 3 years from 2014 till 2017 as process engineer. In 2019, he obtained his master's degree in Energy and Environmental Engineering from KTH Royal Institute, Sweden. In 2020, he joined TU Delft as a researcher and later joined for PhD in the Faculty of Technology, Policy and Management. In 2025, he joined TNO, as a medior scientist and is now working in the Techno Economic Energy Transition Studies Group.

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Looking back at this long and demanding journey, I am struck not only by how much I have learned, but by how many people walked alongside me every step of the way. A PhD is never truly a solo endeavour, and mine was no exception. This journey would not have been possible without the support, guidance, and love of so many remarkable people, and I am deeply grateful to each of them. Each of them, in their own unique way, has left an indelible mark on this work and on who I am today.

First and foremost, I would like to express my heartfelt gratitude to my supervisor, **Andrea**, whose unwavering support, insightful guidance, and endless patience have been my greatest source of strength throughout this journey. From our very first meeting to the final stages of this thesis, your sharp intellect, constructive feedback, and genuine enthusiasm for research have continuously inspired me to think deeper and push further. You challenged me to grow not just as a researcher, but as a thinker and a person. I am fortunate to have had you as my mentor, and the mark you have left on my academic journey will stay with me for the rest of my career.

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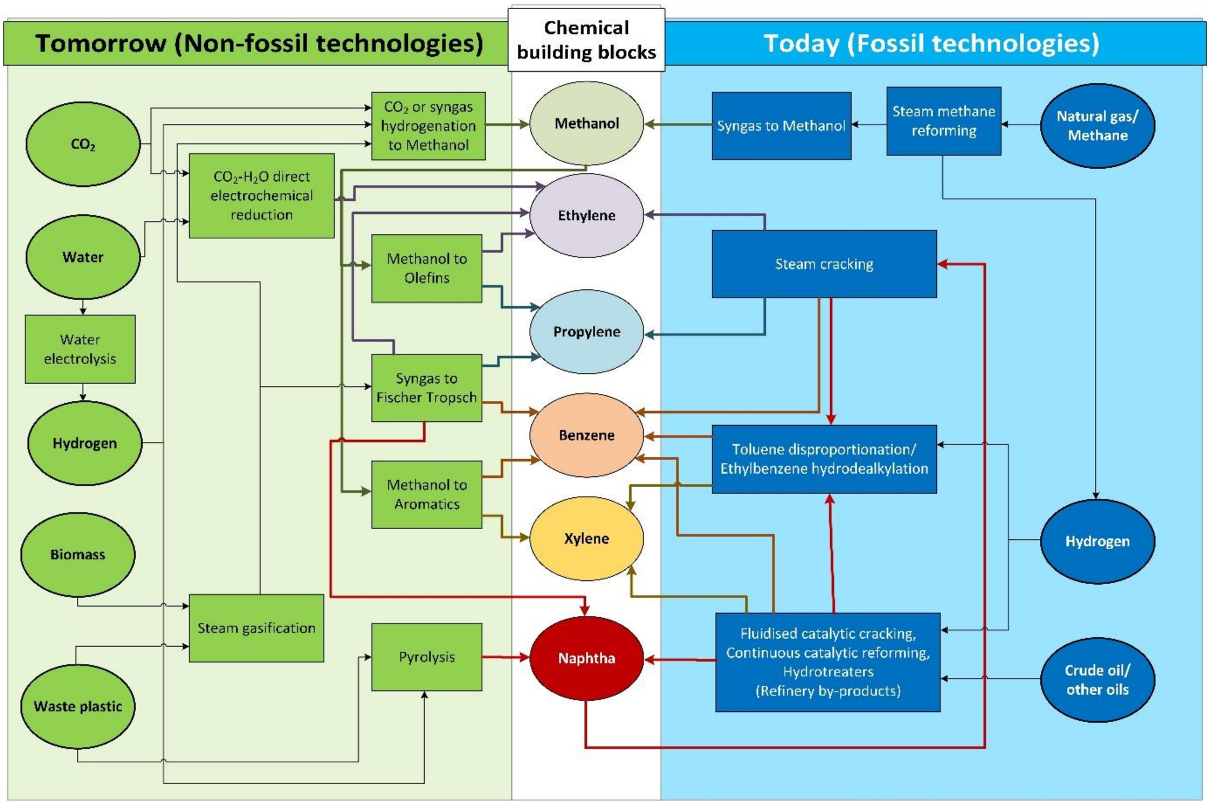
Tomorrow (Non-fossil technologies)
Chemical building blocks
Today (Fossil technologies)
CO_2
Water
Water electrolysis
Hydrogen
Biomass
Waste plastic
CO_2 or syngas hydrogenation to Methanol
CO_2-H_2O direct electrochemical reduction
Methanol to Olefins
Syngas to Fischer Tropsch
Methanol to Aromatics
Steam gasification
Pyrolysis
Methanol
Ethylene
Propylene
Benzene
Xylene
Naphtha
Syngas to Methanol
Steam methane reforming
Natural gas/ Methane
Steam cracking
Toluene disproportionation/ Ethylbenzene hydrodealkylation
Hydrogen
Fluidised catalytic cracking, Continuous catalytic reforming, Hydrotreaters (Refinery by-products)
Crude oil/ other oils