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Ex-Ante Enviro-Economic Assessment of Chemical Production Routes: Computational Tools and Case Studies to Enable Olefins Circularity

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Statement of Originality

I hereby declare that this thesis is my own original work and that all sources have been acknowledged by means of complete references. This work has not been submitted previously, in whole or in part, for any degree or diploma at this or any other university.

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Abstract

Olefins are used in over 70% of all downstream chemical products, making them vital to the chemical industry. However, their current fossil fuel production follows a linear economy model that increasingly conflicts with sustainability goals. A circular economy model proposes replacing fossil fuels with renewable feedstocks, but choosing optimal routes through environmental and economic assessments is complicated and time-consuming. This thesis introduces a computational tool that streamlines enviro-economic assessments for chemical processes modelled in Aspen HYSYS. The tool performs equipment sizing and costing, heat exchange network synthesis, techno-economic assessments, and integrates with existing life cycle assessment software. The tool’s capabilities are leveraged in three case studies investigating routes towards circular ethylene production. The first considers municipal solid waste gasification for producing methanol, ethanol and light olefins. When paired with carbon capture and storage, the gasification route matches incineration costs and benefits from substantially reduced environmental impacts by combining waste management with chemical manufacture. The second case study assessed a novel CO₂-to-ethanol catalyst by designing and modelling a scaled-up process. Whilst the catalyst at its current performance cannot compete with other state-of-the-art CCU routes, addition of a pre-reactor significantly improved performance. Conversion and selectivity targets were determined to direct catalyst development. Finally, the potential for valorising methane side streams in fuel-switched chemical plants was assessed through methanol or ethylene manufacture. Whilst capital costs inhibit potential at lower methane flowrates, profitability is achievable at larger scales with low renewable electricity prices. Environmental benefits are substantial due to utilising waste streams

as feedstock for chemical manufacture. Overall, the developed tool can aid research and development prioritisation efforts in the circular chemical economy.

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Research Outputs

Publications

Chapter 4 is based on the published work:

- **Lyons, B.**, Bernardi, A., Chachuat, B., 2025. *Waste-to-X: Quantifying the environmental performance of chemical production via municipal solid waste gasification*. Sustainable Production and Consumption 57, 167–182.

Chapters 5 and 6 are in preparation for the following publications respectively:

- **Lyons, B.**, Chachuat, B., Al Shaal, G., Ingale, P., Holtze, C., *Ex-Ante Techno-Economic Assessment of a Novel CO₂-to-Ethanol Catalyst*. In preparation.
- **Lyons, B.**, Bernardi, A., Chachuat, B., *To burn or not to burn? An environmental assessment of methane valorisation in a circular economy*. In preparation.

Other Publications

The following publications were also produced alongside the research presented in this thesis:

- **Lyons, B.**, Bernardi, A., Shah, N., Chachuat, B., 2023. *Methane-to-X: an economic assessment of methane valorisation options to improve carbon circularity*, in: Kokossis, A.C., Georgiadis, M.C., Pistikopoulos, E. (Eds.), Computer Aided Chemical Engineering, 33 European Symposium on Computer Aided Process Engineering. Elsevier, pp. 2435–2440.

- **Lyons, B.**, Stanley, S., Bernardi, A., Chachuat, B., 2024. *Waste-to-X: An environmental assessment of circular chemical production via municipal solid waste gasification*, in: Manenti, F., Reklaitis, G.V. (Eds.), *Computer Aided Chemical Engineering*, 34 European Symposium on Computer Aided Process Engineering / 15 International Symposium on Process Systems Engineering. Elsevier, pp. 763–768.

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Chapter 1

Introduction

Historically, the chemical industry has been one of the most important contributors to the UK economy. In 2019, it generated a gross value added (GVA) of £12.6 billion, which corresponds to 6.6% of total manufacturing GVA and 1% of GDP. The sector also employs approximately 99,000 workers mainly in 4 of the industrial chemical clusters throughout the UK (Teeside, Humberside, the North West and Scotland) (Chemistry Growth Partnership and Department for Business, Energy & Industrial Strategy, 2017). When combined with the pharmaceutical sector, the chemicals sector becomes the largest manufacturing exporter in the UK, with total exports exceeding £50 billion per year (Chemistry Council). Olefin production is especially important within the sector as they are used as raw materials in >70% of all organic chemical production (Chen et al., 2017). These olefin derivatives are used to create a significant proportion of consumer goods, including clothing, household appliances, construction materials and packaging (IHS Markit, 2020).

However, the overall chemical sector emits 18.4 million tonnes of CO₂ per year in the UK and olefin production specifically accounts for 25% of these direct sector emissions (Parsons Brinckerhoff and DNV GL, 2015). Not only does olefin production contribute a significant proportion of sector CO₂ emissions, the current linear model (extract, produce, consume, dispose) is unsustainable due to its heavily polluting nature (Korhonen et al., 2018). It is therefore paramount that these issues are addressed as the chemical sector

in its current state is incompatible with the UK’s sustainability policies.

Compounding with these environmental issues is also a recent economic downturn within the UK’s chemical industry. Since 2022, the outputs of other major sectors, such as the pharmaceuticals, automotive, food, and aerospace industries, have either remained stable or risen. By contrast, the output from the chemical sector has fallen by 20% (Chemical Industries Association, 2025). This slowdown in the sector is now starting to affect jobs and confidence in the UK’s ability to manufacture platform chemicals, as closure has now been announced for one of the three steam crackers located in the UK (Conway, 2025).

From both the economic and environmental pressures facing the industry, one thing becomes clear: olefin production in the UK needs innovative solutions to remain a strong contributor to this country’s economy, and to reduce the environmental impacts of one of the foundational chemicals of the whole industry.

One of the proposed solutions to address both of these issues is evolving the UK’s olefin production and overall chemical industry from a linear economy model to a circular economy model. However, this transition cannot be achieved through a simple substitution of individual processes; it requires a systems-level approach that considers the complex network of interconnected feedstocks, conversion technologies, and production pathways available. Rather than isolated process improvements, the shift toward circularity demands simultaneous evaluation of multiple routes to identify which combinations offer the greatest potential for sustainable olefin production.

1.1 Circular Economy

The circular economy has been proposed as a solution to the current need to move towards a more sustainable society. Whilst there is no scientifically agreed upon definition of what a circular economy is, Geissdoerfer et al. (2017) suggested the following:

[A] regenerative system in which resource input and waste, emission, and energy leakage are minimised by slowing, closing, and narrowing material and

energy loops. This can be achieved through long-lasting design, maintenance, repair, reuse, re-manufacturing, refurbishing, and recycling.

A representation of a circular economy is also illustrated in Figure 1.1, which highlights the closing of material loops and the minimisation of leakage into the environment. The

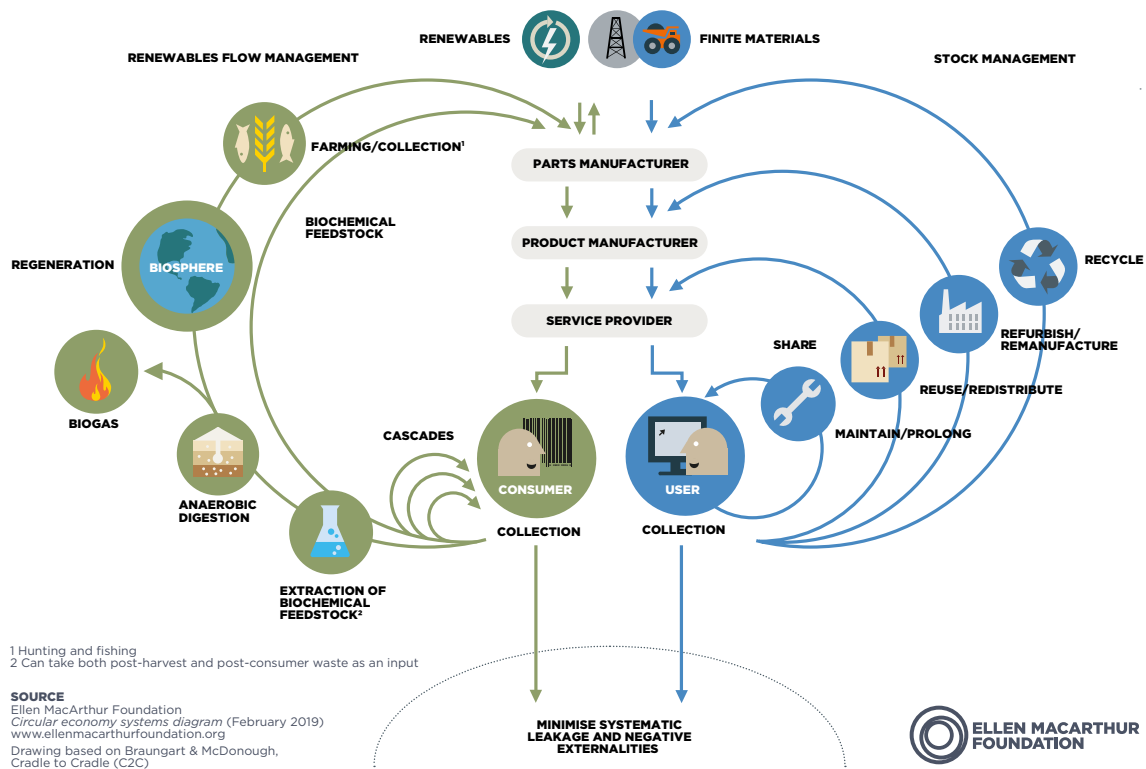


Figure 1.1: Butterfly diagram illustrating a circular economy (Ellen Macarthur Foundation, 2019a)

Ellen Macarthur Foundation also proposes that there are three main principles that a circular economy adheres to: eliminating waste and pollution; circulating products and materials; and regenerating nature (Ellen Macarthur Foundation, 2022). Many view the global natural ecosystem as a desired vision for a circular economy; one where no material is wasted and the only input is the renewable (and essentially infinite) source of energy from the Sun (Korhonen et al., 2018).

However, the implementation of a circular economy from the current linear model has many challenges. Korhonen et al. (2018) summarised six main barriers to a circular economy:

1. **Thermodynamic limitations** - due to the second law of thermodynamics, recycling will always require energy.
2. **System boundaries** - both spatial and temporal boundaries must be considered to avoid burden shifting.
3. **Path dependency** - also known as 'survival of the first' where new technologies must compete with decades of efficiency improvements in current technologies.
4. **Rebound effects** - improving the efficiency of a materials production will reduce its price and in turn will increase its consumption.
5. **Social concept of waste** - influences how waste streams can be managed and collected.
6. **Governance** - difficulty in proposing policies that are harmonious between industries and regions.

These issues illustrate that care must be taken when converting to a circular economy. Just because a system is circular does not mean it is inherently better environmentally (Harris et al., 2021). Additionally, it is difficult to quantify the circularity of a system, with a vast number of different circularity indicators presented in the literature across many different categories (including different scales i.e. micro, meso, macro and performance metrics) (Saidani et al., 2019).

1.2 Circular Chemicals

The interest in a circular economy has grown rapidly within the chemical industry over the past decade, as illustrated in Figure 1.2.

The literature reveals that a circular economy will be paramount in the transition towards sustainable chemicals, with a recent report suggesting that a circular economy would reduce chemical demand by 29-31% by 2050 (SYSTEMIQ, 2022). However, there are three specific challenges for the chemical industry in moving towards a sustainable

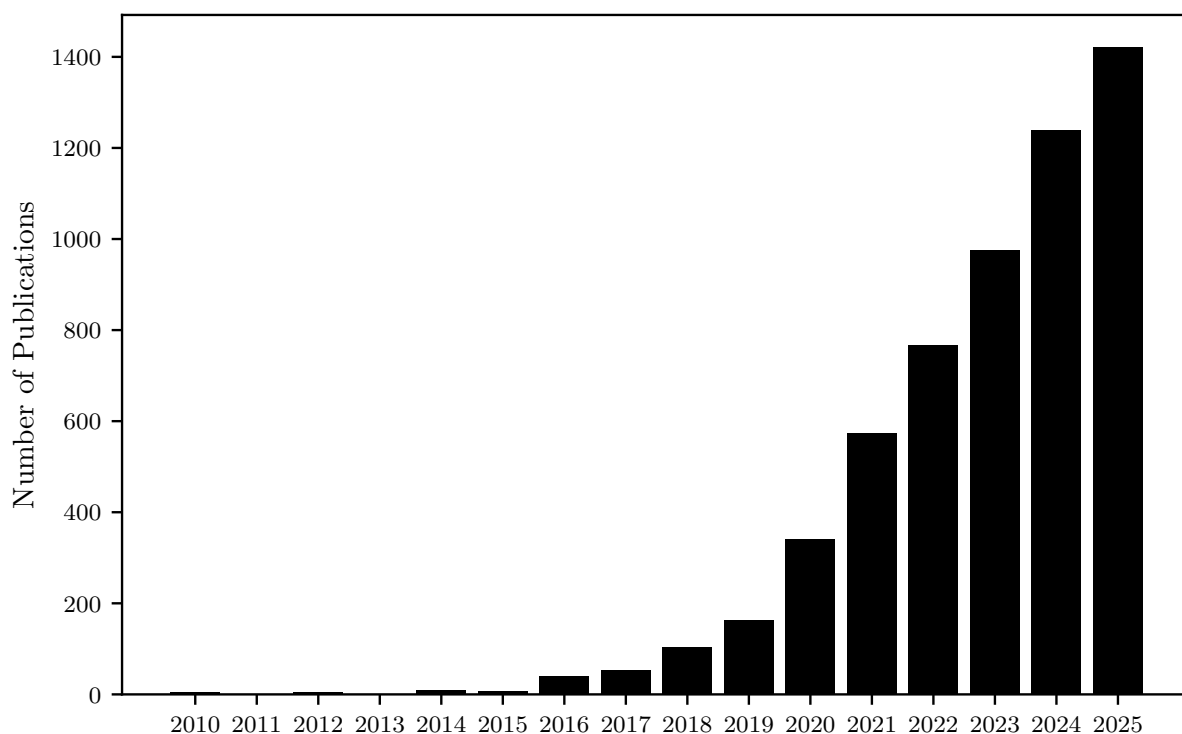


Figure 1.2: Number of publications per year containing "circular economy" as keywords within Chemical Engineering subject area (from www.scopus.com) as of September 2025.

and circular economy: reducing CO₂ emissions of processes and utilities; switching of feedstock; and increasing recycling (Lange, 2021). The first point is focused on achieving net-zero (through fuel switching to H₂, electrification etc), but the last two are both concerned with circularity. Switching to renewable feedstocks (i.e. mixtures of biomass, CO₂ and solid wastes) is theoretically possible to minimise the reliance of new fossil feedstocks as long as high recycling rates are achieved (Meys et al., 2021). At first glance, using biomass and CO₂ as feedstock in the chemical industry does not appear to be directly circular. However, if chemical products are either decomposed or combusted to release CO₂ into the atmosphere, this carbon can be captured and recycled either through the growth of biomass and CO₂ capture from either point sources or directly from the air. A downside of these outer loops though is that they typically require more energy (Mihelcic et al., 2003).

It is also important to distinguish between decarbonisation and defossilisation when considering the chemical industry's transition. Decarbonisation focuses solely on reduc-

ing CO₂ emissions, which could theoretically be achieved through carbon capture and storage on existing fossil-based processes. Defossilisation, however, requires the complete removal of fossil carbon from the feedstock, necessitating a switch to renewable or circular carbon sources such as biomass, waste, or captured CO₂ (Hutchings, 2024). Whilst decarbonisation addresses the symptom (emissions), defossilisation addresses the root cause (fossil resource dependence), thereby potentially achieving both environmental sustainability and improved resource efficiency.

With multiple potential circular feedstocks to utilise, and many conversion technologies available at various levels of technology readiness, it is difficult to identify which routes should be prioritised for development and implemented at scale. An ex-ante approach (assessing prospective environmental and economic performance prior to commercial deployment) is therefore essential for guiding research and development efforts, as it allows the identification of promising pathways and potential barriers before substantial capital investment is committed. This reduces the risk of misdirecting resources toward uncompetitive routes and provides actionable insights to guide the chemical industry towards the most sustainable and economically viable pathway.

1.3 Thesis Objectives

The general aims and objectives of this thesis are summarised as follows:

- Identify routes and feedstocks that could enable circular ethylene production.
- Create a systematic framework that allows quick and reliable environmental and economic assessment (EEA) of these routes.
- Explore economic scenarios where these routes are most competitive and viable against the current fossil-fuel based manufacturing routes.
- Confirm if the identified circular production routes offer environmental benefits over the linear economy model.

1.4 Thesis Outline

The thesis is structured as follows:

- In Chapter 2, the relevant background is presented in a literature review. This entails both an overview of potential production routes and feedstocks for circular ethylene production, as well as the methodology required to perform environmental and economic assessments on these routes. This chapter also summarises the identified gaps in the current literature, and the contributions of this thesis that are presented in the subsequent chapters.
- In Chapter 3, a new computational tool is introduced that streamlines environmental and economic assessments of chemical production routes. The tool forms the methodological basis for all assessments performed in this thesis, and its benefits and capabilities are demonstrated through a short case study investigating ethylene production via bioethanol dehydration.
- In Chapter 4, the economic and environmental performance of coupling municipal solid waste gasification as a waste management solution with platform chemical manufacture is assessed.
- In Chapter 5, a novel process is designed for a lab-scale, single-step, CO₂-to-ethanol catalyst, and its economic performance is assessed within the context of a larger olefins value chain. Additionally, catalyst development targets are quantified to improve the catalyst's competitiveness.
- In Chapter 6, the potential for utilising methane by-product streams for chemical manufacture is investigated, where originally these streams were combusted as a fuel source.
- Finally, Chapter 7 concludes the thesis, summarising the main contributions and outlining directions for potential future research.

Chapter 2

Background

2.1 Ethylene Production Routes

2.1.1 Steam Cracking

Currently, ethylene is predominantly manufactured via a process called steam cracking. This process adds steam to either a gaseous or liquid saturated hydrocarbon feedstock (e.g. ethane or naphtha) and converts it to olefins (Sadrameli, 2015). This is a highly endothermic reaction and requires high energy input rates, which is achieved in the cracker unit, the most important section in the steam cracking plant (Zimmermann and Walzl, 2009). The cracker unit is split into three main sections: the radiation section or firebox; the convection section; and the stack. In the radiation section, the cracking reaction takes place inside tubular reactors placed in the centre of the firebox, which are surrounded by floor and/or wall burners. The fuel used in the burners is typically methane produced from the cracker unit itself, and temperatures in the firebox are between 750-900°C. The convection section is primarily used for feed pre-heating, but is also used for high pressure steam generation. This section has become more thermally efficient over the past few decades: old cracker units had flue gases leaving the stack at around 400°C; modern units have flue gases leaving the stack at around 100 °C (Sadrameli, 2015).

A steam cracking plant contains 3 other main sections after the cracker unit: the quench section; compression section; and separation section (Fakhroleslam and Sadrameli,

2019). In the quench section, the gaseous products from the cracker unit are rapidly cooled to prevent unwanted side reactions and to maximise the yield of desired products. This rapid cooling is achieved in special heat exchangers known as a transfer line exchangers (TLE), which cools the gas from 850°C to 300-425°C in a fraction of a second by producing high pressure steam. The gas is further cooled to ambient temperatures in direct quench towers after the TLEs. The next section is the compression stage, where the pressure of the gas is increased to 40-50 bara in preparation for the separation section. This is achieved via multistage compression with interstage cooling and knockout drums to remove any remaining water or liquid hydrocarbons. This section will also contain an acid gas removal unit. Finally, there is the separation section, which uses cryogenic distillation columns to separate the products from each other. This distillation train will typically start with a de-methaniser, then followed by a de-ethaniser, C2 splitter (for separating ethylene from ethane), de-propaniser and a C3 splitter. Depending on the feedstock used, other columns such as a de-butaniser and de-pentaniser may be needed as well. The order of these separation units can also be optimised depending on the feedstock.

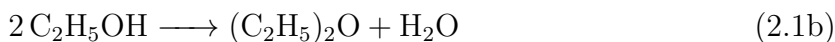
Despite the maturity of the steam cracking process, ethylene production accounts for a significant portion of CO₂ emissions in the UK's chemical industry. This is because steam cracking is the most energy intensive process in the chemical industry, and consumes 8% of the sector's total energy use globally. The cracker unit alone consumes 65% of the overall process energy (Ren et al., 2006) and accounts for 90% of the CO₂ emissions. This intensive process results in steam cracking emitting between 1-1.6 tonnes of CO₂ per tonne ethylene produced (depending on the feedstock used) (Amghizar et al., 2020).

Different options are available to decarbonise steam crackers, which include using alternative feedstocks (e.g. oil derived from biomass or plastic waste pyrolysis) or switching the fuel in the cracker to hydrogen. A recent development is the roto dynamic reactor, which aims to electrify the steam cracking process. This reactor consists of an electrically driven motor which supplies thermal energy to the steam and hydrocarbon feed through high velocity rotor blades instead of combusting fuel in a furnace (Seppala et al., 2018).

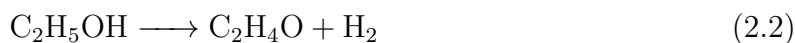
This reactor allows for shorter residence times and higher temperatures, which leads to higher ethylene yields (Coolbrook).

2.1.2 Ethanol Dehydration

Another ethylene production route is the dehydration of ethanol. The main reaction scheme is comprised of two reaction pathways: a direct pathway and an indirect pathway. The direct pathway is the direct dehydration of ethanol to ethylene as illustrated below in Equation 2.1a. The indirect pathway goes through di-ethyl ether (DEE) as an intermediate product as shown in Equations 2.1b and 2.1c (Morschbacker, 2009).



The indirect pathway is favoured at lower temperatures, between 150-300°C, where the direct pathway is favoured at higher temperatures up to 500°C. Acetaldehyde is also formed as an unwanted side product.



The first stage in the ethanol dehydration route to ethylene is the production of ethanol from biomass, which consists of 4 main stages. The first is grinding and milling, which crushes the biomass into coarse particles. The next step is liquefaction and saccharification. Here, enzymes are added to the biomass along with water to form a mixture called 'mash'. Starch within the mash undergoes enzymatic hydrolysis which breaks it down into simple sugars. This stage can be skipped with certain types of biomass if the sugars can be extracted directly from the crop e.g. sugar cane. Afterwards, yeast is added to the mixture in the fermentation stage. Under anaerobic conditions, the yeast converts

the sugar into ethanol and CO_2 . The final stage is distillation and drying, where the ethanol is separated from the fermentation solution (Naik et al., 2010). Non-fermentable solids are also separated from the ethanol, which are then dried to form a product known as dried distiller's grain with solubles or DDGS. DDGS is high in protein and is commonly sold as a nutritional animal feed (Wood et al., 2014).

After the ethanol has been produced, it can be fed to the ethanol dehydration process which consists of 3 stages: a reaction stage; recovery stage; and a purification stage. In the reaction stage, the ethanol is reacted in vapour phase in fixed bed reactors over an alumina based catalyst. Due to the highly endothermic nature of the reaction, it is common to use multiple adiabatic reactors in series with re-heating between the reactors, with temperatures between 300-500°C showing the highest selectivity towards ethylene (Mohsenzadeh et al., 2017). After the reaction section, the products are cooled and sent to the recovery section. Here, a direct water quench tower removes the bulk of the produced water and the products are then sent to a compression train. The compressors have interstage cooling and flash separation vessels for the removal of any remaining water and ethanol. A caustic wash and dryer is used to remove any final traces of CO_2 and water. The pressure in this section is increased to approximately 30 bara for the final purification stage. Here, cryogenic distillation is used to obtain polymer grade ethylene (99.9%) and separate out the side products (Becerra et al., 2017).

The ethanol dehydration process for the production of ethylene is already commercialised, with the majority of the world's capacity currently in Brazil, where sugarcane is available as a cheap feedstock for ethanol production. Three plants are currently in operation in Brazil, with a total ethylene capacity of 600 kt/y. However, this only corresponds to approximately 0.49% of the world's total ethylene production capacity (Jamil et al., 2022).

2.1.3 Methanol-to-Olefins

Methanol to hydrocarbon reactions were first discovered in the 1970s with ZSM-5 catalysts. A decade later, Union Carbide scientists created a silicoaluminophosphate molecu-

lar sieve catalyst known as SAPO-34, which had a high selectivity towards ethylene and propylene. The development of this catalyst was crucial in commercialising the methanol-to-olefins (MTO) process. The main characteristic of the SAPO-34 catalyst is its very small pore size (5 angstroms on average), which lead to a high selectivity towards the smaller olefins (Chen et al., 2005).

The overall reaction stoichiometry for the process can be represented as follows (Gogate, 2019):



Where the main products are ethylene and propylene (75-80wt% on a dry basis) and higher olefins (C4+ at 10-15wt%). Other products formed include alkanes, some hydrogen, CO, CO₂ and coke (Kuechler and Lattner, 2000). This global reaction is highly exothermic, releasing approximately 850 kJ per kg of methanol at 500°C (Dimian and Bildea, 2018). The reaction takes place in a fluidised bed reactor connected to a regenerator, where the catalyst is continuously sent to burn off the coke. Reaction conditions are 340-500°C and between 1-3 bara and conversion of methanol is close to 100%. Steam generation is used to control the heat of reaction. After the reactor, the product is cooled and the water is separated. CO₂ removal steps and a dryer are subsequently used to remove any trace amounts of CO₂ and water, before the products are sent towards a typical olefin separation section (Keil, 1999). A diagram of the MTO process is presented in Figure 2.1.

UOP and Norsk Hydro are the current global leaders in MTO commercial licensing, but a recent development is the olefin cracking process (OCP) by Total Petrochemicals. This is a catalytic cracking process that cracks the C4+ olefin stream into additional ethylene and propylene, which are the higher value products (Glover, 2007). The addition of an OCP section can increase the overall C2/C3 yield to 85-90wt% and can decrease the C4+ stream by 80%, which represents a substantial increase in revenue (Vora and Pujado, 2010). The OCP also has a higher selectivity towards propylene, so it can be used to adjust the overall ethylene to propylene ratio in the MTO process. For MTO by itself, the ratio is typically around 1, however in the OCP, it is 3.5-4 towards propylene which

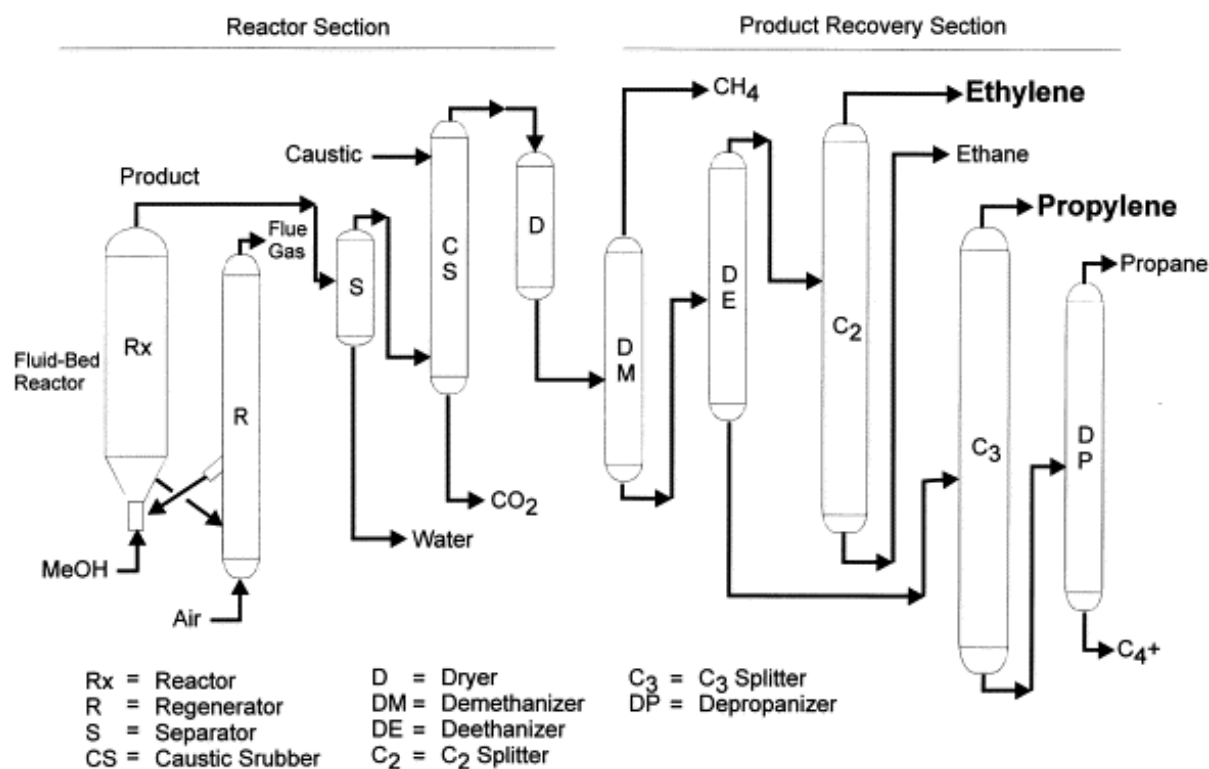
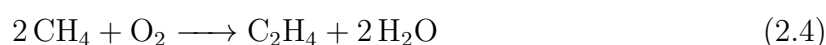


Figure 2.1: Diagram of the MTO process (Keil, 1999)

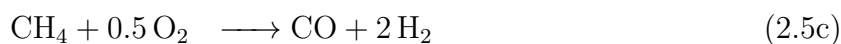
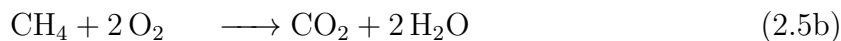
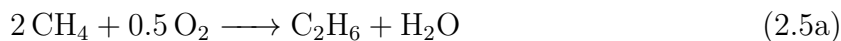
leads to an overall propylene to ethylene ratio of 1.3-2 for the combined process (Hannula and Arpiainen, 2015a). This route becomes particularly relevant for circular production when methanol is derived from waste feedstocks via gasification or CO₂ hydrogenation.

2.1.4 Oxidative Coupling of Methane

In 1982, Keller and Bhasin (1982) first proposed the oxidative coupling of methane (OCM) as a potential route for the production of ethylene directly from methane. They investigated the formation of ethylene and ethane from methane over different metal oxide catalysts at temperatures between 500-1000°C and suggested that the route would overcome the highly endothermic nature of the current ethylene production routes. OCM has since been the subject of high industrial and academic interest. In the overall reaction, methane reacts with oxygen with the aid of a metal oxide catalyst to form ethylene and water and is an exothermic reaction (Chung et al., 2016):



However, there are additional parallel reactions that occur during OCM (Cruellas et al., 2019):



The formation of ethane is the primary step in OCM, whereas the complete and partial combustion of methane to form CO and CO₂ are unwanted side reactions. The high temperatures needed to break C-H bonds leads to increased selectivity towards the unwanted combustion reactions. This conflict is what has limited the progress in making OCM a commercial process, as it currently presents low yields and low selectivities towards the formation of C₂ compounds thanks to these unavoidable side reactions (Layritz et al., 2021).

Despite decades of research, the commercialisation of OCM has been challenging due to these low yields of C₂ compounds, which are typically around 20% (Stansch et al., 1997). However, chemical looping is garnering increased interest for use in OCM. In a chemical looping OCM (CLOCM), methane and metal oxide catalyst are fed together in one stage of the loop where the oxidative reactions take place, then the catalyst is re-oxidised in another stage of the loop. Figure 2.2 shows a representation of this CLOCM arrangement (Damasceno et al., 2022). CLOCM is being pursued since it offers a distinct advantage over the more traditional co-feed reactor configuration. In the co-feed arrangement, oxygen is present in both gaseous form and lattice form within the metal oxide catalyst. However, CO_x formation is mainly caused by reactions between the carbon compounds and gaseous oxygen. In CLOCM, oxygen is only supplied as lattice oxygen, which can reduce the formation of CO_x products and increases the selectivity towards C₂ formation (Parishan et al., 2018).

Several types of catalysts have been investigated for use in CLOCM, including magnesium manganese catalysts, rare-earth oxides, and perovskite-type catalysts (i.e. catalysts

of the form ABO_3 (Wenk and Bulah, 2016)). Studies with the CLOCM arrangement have shown promise with these types of catalyst, with yields approaching or at 30% for C2 components (Sung et al., 2010; Baser et al., 2021). However, challenges still remain with finding a catalyst with a high enough catalytic activity, whilst remaining stable over multiple redox cycles as is inherent in the CLOCM arrangement. When paired with sustainable methane sources such as biogas, OCM offers a potential pathway for circular ethylene production from waste-derived feedstocks.

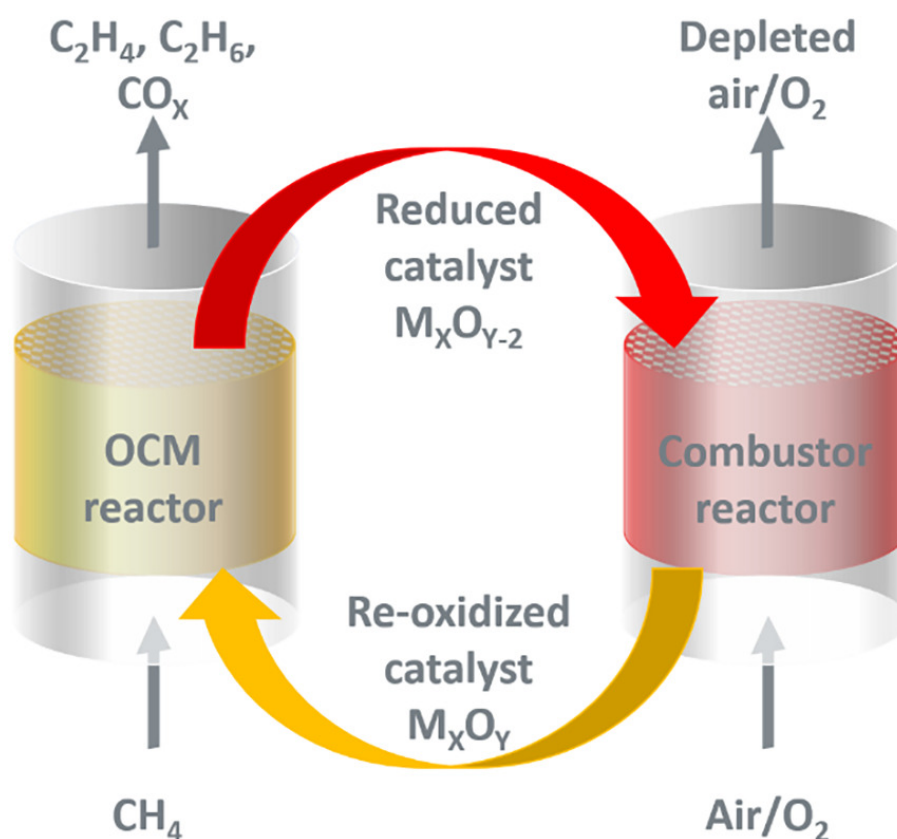


Figure 2.2: Diagrammatic representation of oxidative coupling of methane in a chemical looping design (Damasceno et al., 2022)

Whilst commercialisation of OCM remains challenging, the route represents a potential valorisation pathway for methane feedstocks, linking to a broader circular chemical economy strategy.

2.2 Waste Feedstocks for Circular Ethylene

The ethylene production routes described above can be supplied by a range of waste-derived feedstocks through intermediary conversion processes such as gasification and pyrolysis, with plastic waste representing the most significant opportunity for circular chemical production. One study showed that in 2013, 40% of fossil fuel inputs (including coal, natural gas and oil) was used to manufacture thermoplastics (including polyethylene, polypropylene, polyvinylchloride, polystyrene and polyethylene terephthalate) (Levi and Cullen, 2018). Therefore, it is intuitive that a large portion of the renewable feedstocks that are needed in a circular chemical economy would ideally come from recycled plastics.

Plastic waste is one of the most visual forms of waste from the chemical industry that the general public interact with every day. Figure 2.3 shows the current plastic flows per 100t produced. Over 70% end up leaking into the environment or dumped into landfills. 14% is incinerated, which is more environmentally friendly than landfilling, but will result in additional CO₂ emissions if they are not captured. Only 14% of plastic is recycled, 4% of which is lost, 8% is used in cascaded or open recycling and only 2% is used in closed loop recycling (Li et al., 2022). This emphasises the need to improve recycling technologies and increase recycling rates. IHS Markit analysis predict that of the \$1.5 trillion required by the plastic industry to meet global demand in 2050, at least \$300 billion should be used for both mechanical and chemical recycling technologies (IHS Markit, 2021).

2.2.1 Plastic Recycling Categories

There are 4 main categories of plastic recycling: primary; secondary; tertiary and quaternary (Singh et al., 2017; Schwarz et al., 2021).

1. **Primary recycling** is the recycling of material that leads to a product that is almost identical to a product formed from virgin material. It is also known as closed loop recycling. To ensure the new product maintains the original properties, the plastic must be uncontaminated and only of a single type.

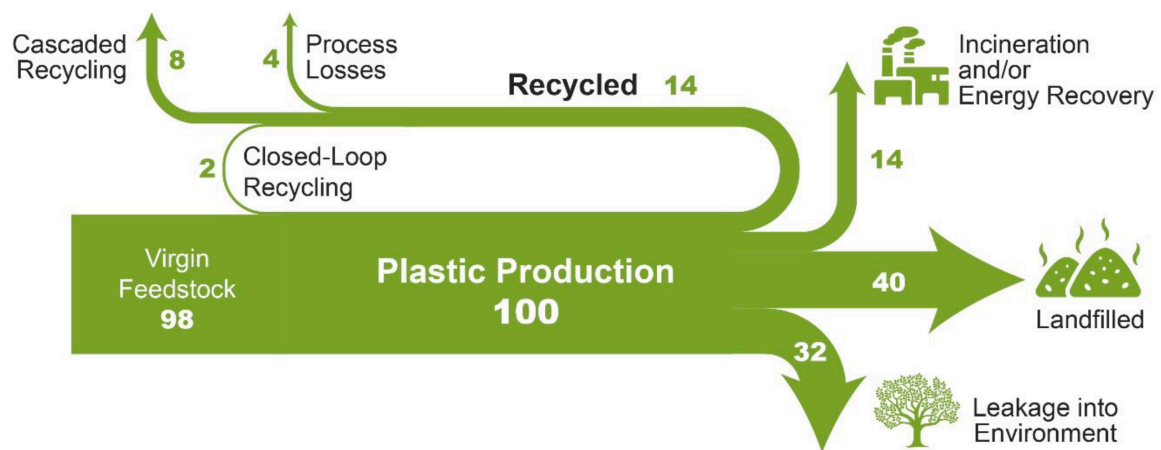


Figure 2.3: Sankey diagram of global plastic flows (Li et al., 2022)

2. **Secondary recycling** is the mechanical reprocessing of plastic material to form new products. It is also known as open-loop recycling or down cycling as the new product cannot be used in the original application due to loss of mechanical properties.
3. **Tertiary recycling** encompasses chemical recycling, where the plastic waste is broken down to form valuable products via thermal or chemical means.
4. **Quaternary recycling** involves the combustion of plastic waste as an alternative to landfilling. Although the plastic is destroyed, heat and electricity can be recovered in the incinerator.

Primary and secondary recycling both rely on mechanical recycling technologies and is the most common approach for recycling plastic waste currently. There are common steps between the two categories after sorting of the plastic waste in secondary recycling: shredding and granulation; contaminant removal; flake segregation (polymer flakes are more difficult to process compared to granules); and the main step, melting and extrusion, where the polymer is converted into new plastic pellets (Jagtap et al., 2015). However, plastic cannot be mechanically recycled indefinitely. Each time plastic is reprocessed, it undergoes three main forms of degradation (Ragaert et al., 2017):

- **Thermal-mechanical degradation:** This is degradation due to the heat and mechanical stress on the polymer during its re-extrusion. These stresses can cause the polymer to undergo chain scission, which breaks the polymer chain and reduces its molecular weight.
- **Mixed stream processing:** This only applies to secondary recycling, where a mix of plastics with different melting points can be reprocessed together. To melt the plastic mix in the extruder, the temperature must be above that of the highest melting point plastic, which may far exceed that of the lowest melting component. This in turn leads to additional thermal degradation of the material.
- **Lifetime degradation:** This is degradation due to exposure to different stressors

during the plastic's use phase. This can include heat, moisture, radiation, and oxygen.

Once a polymer has gone through several mechanical reprocessing cycles, it should then undergo tertiary or chemical recycling. Two of the most common thermal-based chemical recycling routes will now be focused on: pyrolysis and gasification.

2.2.2 Pyrolysis

Pyrolysis is the decomposition of organic compounds in an oxygen-free, high temperature environment (Rollinson and Oladejo, 2020). The products are normally a mixture of gases, oils, waxes and some char, with higher temperatures favouring the production of gaseous and liquid products (Li et al., 2022). Overall composition and yield of plastic waste pyrolysis is highly dependant on multiple variables, including feed composition, reactor type and process conditions. Typical temperatures are between 350-700°C, but studies have shown that only gas and oil fractions can be obtained above 600°C (Al-Salem et al., 2010). The main advantage of pyrolysis is its ability to breakdown a variety of plastics into products with lower molecular weight, including fuels and in some cases, the plastic monomers themselves (Jeswani et al., 2021).

Many studies have investigated pyrolysis as a potential chemical recycling route for plastic waste. Fivga and Dimitriou (2018) performed a techno-economic analysis on a plastic waste pyrolysis plant located in the UK . The proposed plant was modelled in Aspen Plus, with a mixed feedstock of polyethylene, polypropylene and polystyrene. The plants aim was to transform the plastic waste into a heavy fuel oil substitute. The authors modelling a fluidised bed reactor at 500°C to produce a gas and char product based on experimental yields from a UK recycling company. Economies of scale were found to be of large importance to the profitability and competitiveness of the plant. Above 20t/h, the price of producing the fuel oil substitute was many times smaller than the fossil alternative.

Gracida-Alvarez et al. (2019) performed a TEA on an HDPE pyrolysis plant modelled in Aspen Plus. The plant produced a range of products: ethylene, propylene, aromatics

and both a low and high molecular weight hydrocarbon mixture (LMWHC and HMWHC respectively). The LMWHC was mainly C3-C10 compounds, the HMWHC was C11+. The yields in the pyrolysis reactor were based on experimental results from the authors previous work. The results of the TEA revealed that the plant had a discounted cash flow rate of return (DCFROR) of 31%. A local sensitivity analysis on the NPV of the overall plant revealed that the NPV was most sensitive to the interest rate and the LMWHC price. This was to be expected since the LMWHC stream accounted for 53% of the overall product mass flow. The results also suggest that a multi-product pyrolysis plant could be highly profitable .

Larrain et al. (2020) also performed a TEA on a pyrolysis plant using mixed polyolefins (MPO) as the waste feedstock. The yields were based on industrial data and two scenarios were considered: an open loop option which produced both naphtha and wax; and a closed loop option which only produced naphtha. The change in product distribution between the two options was achieved by adjusting the operating pressure, with the higher pressure resulting in lower wax production. The results of the TEA revealed that the open-loop option was more attractive economically due to the high value of wax compared to naphtha. The authors also found that the plant capacity of both options must be above a minimum value to be profitable: 120 kt/y for the closed loop plant; and 70kt/y for the open loop plant. A sensitivity analysis was also performed and found that feedstock availability (i.e. operation time), CAPEX and product prices were the most influential parameters to the net present value.

Somoza-Tornos et al. (2020) performed both a TEA and LCA on a high temperature pyrolysis plant for the production of ethylene. The plant used approximately 450 ton/day of purified LDPE feedstock to produce methane, ethylene, propylene, benzene as the main products, along with other side products which were used as fuel for the pyrolysis reactor. The results revealed that ethylene from the pyrolysis plant is both more economical and more environmentally friendly compared to the equivalent from steam cracking. The price per kg of ethylene was 54% cheaper in the pyrolysis plant and the end point LCA indicators revealed a 87%, 88% and 164% reduction in end point impacts to human

health, ecosystem quality and resource scarcity respectively. The authors also performed an LCA comparison from the plastic waste perspective, comparing the pyrolysis of the waste to incineration and landfilling. The pyrolysis process was again found to have lower environmental impacts than both end-of-life options.

Thunman et al. (2019) presented an interesting case study looking at switching a chemical cluster from fossil feedstocks to plastic waste in Sweden. The authors investigated the switch over 4 proposed stages: 1) the partial replacement of feedstock with the construction of a plastic waste pyrolysis reactor 2) the complete replacement with plastic feedstock 3) the electrification of the process and reactors and 4) the introduction of oxy-combustion and carbon capture for maximum carbon recycling. Stage 2 results in an excess of fuel gas being produced, which is converted to additional olefins via steam reforming to product syngas, which is then used in a methanol-to-olefins (MTO) pathway. An alternative pathway using biomass as a feedstock instead of plastic was also considered. The authors found that the first two stages were economically attractive without any external incentives. The final two, however, only made economical sense if environmental credits were applied to the cluster e.g. for CO₂ savings and for increasing the amount of biogenic carbon in the plastic products. The CO₂ savings were only realised in these final two implementation steps though.

Despite the promising results the TEA and LCA studies described above have shown, the reality of implementing plastic waste pyrolysis on a large scale is challenging. The main issue is that pyrolysis oil, one of the main products obtained from plastic waste pyrolysis, is not equivalent as a naphtha substitute as is assumed in many of these studies (Li et al., 2022). Fig 2.4 shows that naphtha is mainly comprised of alkanes and 10% aromatic compounds. A typical pyrolysis oil from plastic waste contains primarily olefins and cycloalkanes over a much wider range of carbon numbers. Not only that, but if the feedstock is not appropriately cleaned, contaminants present in the oil are far beyond the acceptable limits for further chemical processing (Kusenberget al., 2022). These contaminants include nitrogen, oxygen, chlorine, iron and calcium and can lead to downstream corrosion, fouling and catalyst poisoning. Significant upgrading and cleaning of the oil

would be required before use in existing crackers.

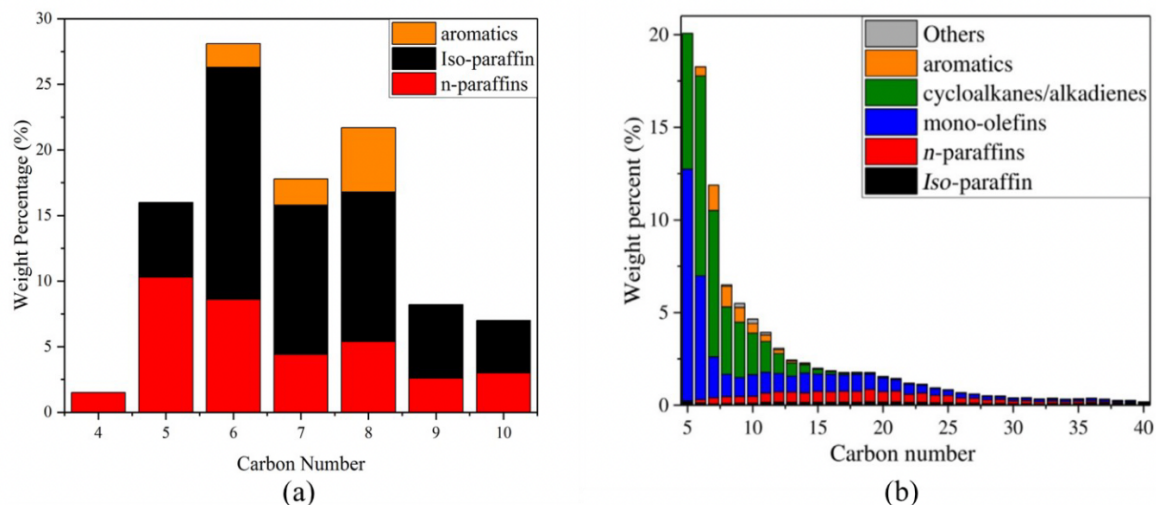


Figure 2.4: Composition comparison between typical (a) naphtha and (b) pyrolysis oil (Li et al., 2022)

2.2.3 Gasification

Gasification is the partial thermal oxidation of an organic feedstock. It yields a mixture of CO , H_2 , CO_2 , CH_4 along with solid residue (i.e. ash) (Puig-Arnau et al., 2010). Different oxidising agents can be used, including air, steam or pure oxygen. The syngas or hydrogen component that is produced in gasification can either be burned as fuel if it is of a low quality (i.e. low H_2 ratio) or used as a feedstock for many chemical processes. Fischer-tropsch uses syngas for fuel production, methanol from syngas is a precursor for many other chemicals and hydrogen can be used in the Haber-Bosch process for fertiliser production (Wender, 1996).

A critical advantage that gasification has over pyrolysis is its relative independence of product distribution from feedstock composition. The product yields from pyrolysis are highly variable, especially when considering mixed feedstocks such as plastic waste, but also municipal solid waste and biomass wastes. In gasification, a different feedstock composition will vary the relative gaseous composition and minor side product yields, such as char and tar, but not the obtained compounds. Different levels of gas cleaning may be required though depending on the feedstock (Lopez et al., 2018).

To the best of the authors knowledge, there have not been as many TEA and LCA studies on the gasification of solid wastes when compared to pyrolysis. Bora et al. (2020) compared the gasification of waste polypropylene to incineration and landfilling via a TEA and LCA. The final product of the process was the syngas, which was sold directly. The authors found that gasification outperformed incineration and landfilling in most midpoint LCA categories, including the global warming potential (GWP). It was also highly profitable assuming a plant lifetime of 20 years.

Arena et al. (2015) performed a TEA on the gasification of packaging derived fuel (PDF) for a waste-to-energy plant. They looked at three different end-use scenarios for this energy recovered in this plant: power generation; combined heat and power; and district heating. The PDF was composed of primarily plastic-based materials and had the following main elemental composition: 59wt% C, 7.7wt% H₂ and 26wt% O₂. They also considered the presence of contaminants, including chlorine and sulphur. A bubbling fluidised bed gasifier was used alongside an internal combustion syngas optimised engine for the power generation. Results indicated that the internal rate of return (IRR) was 0.5% for power generation, 18.9% for district heating, and 29.8% for combined heat and power.

Voss et al. (2021) compared processing municipal solid waste (MSW) in a chemical recycling facility to incineration in Germany. The chemical recycling facility consisted of two parts: anaerobic digestion to process the organic fraction of the MSW, which was used in a combined heat and power plant; and a gasification section, which converted the remaining MSW fraction into refuse derived fuel (RDF). The RDF was gasified to produce syngas, which was then subsequently used to produce methanol and finally olefins. The authors found that in a base case economic scenario of a 76 kt/y plant, it was not profitable and less economically attractive compared to the incineration plant. However, the economic performance of the chemical recycling facility was found to be highly dependant on its scale and when combined with tighter environmental regulations and favourable market conditions, it can become profitable.

2.2.4 Circular Ethylene Route Map

The routes discussed in this chapter, particularly those involving plastic and municipal solid waste, can be situated within a broader circular ethylene production landscape. Figure 2.5 presents an overview of potential pathways from multiple feedstocks (municipal solid waste, plastic waste, CO₂, and methane) through various intermediate chemicals to ethylene production. Whilst plastic waste has received the most research attention as a circular feedstock, these alternative sources represent complementary pathways that will be explored in subsequent chapters of this thesis.

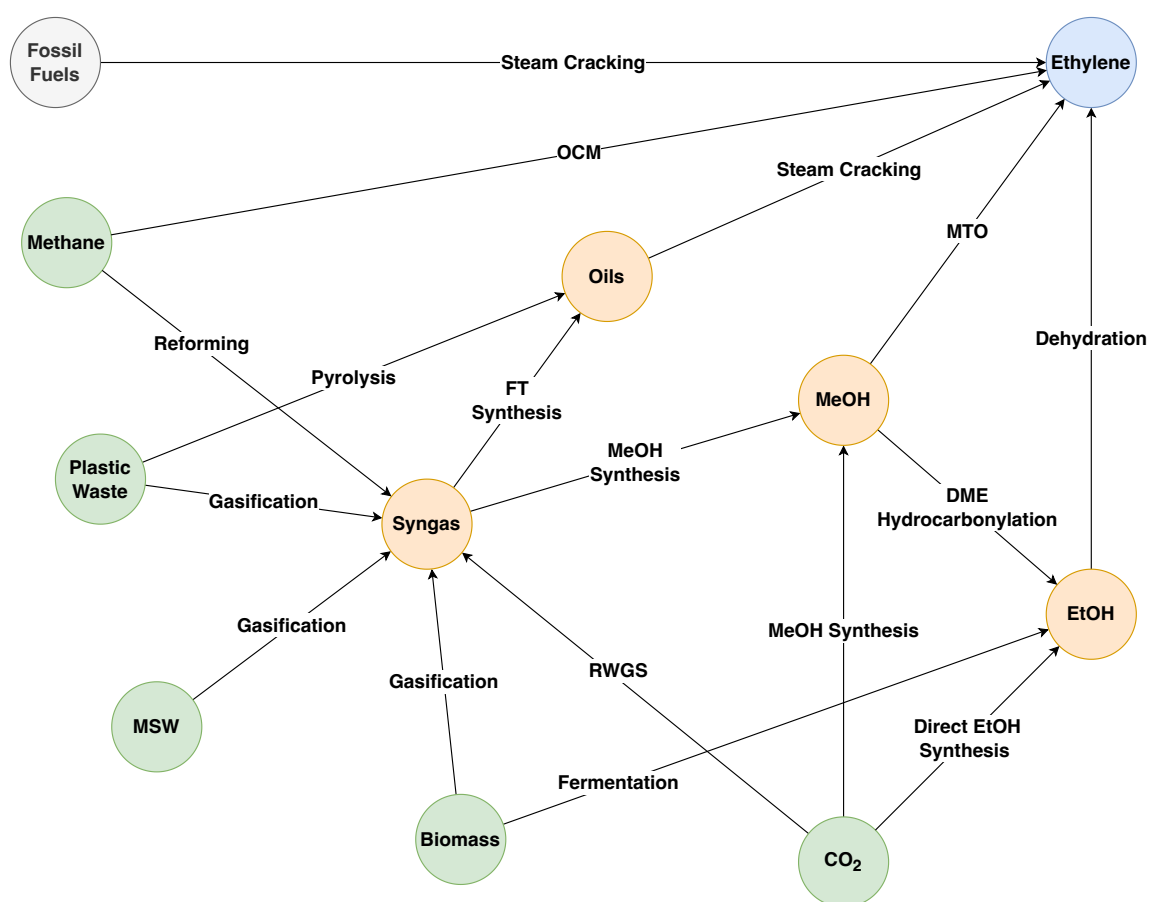


Figure 2.5: Overview of potential routes for circular ethylene production.

The assessment of these diverse circular routes requires systematic enviro-economic evaluation frameworks. The following section outlines the methodologies employed to quantify both the economic performance and environmental impacts of circular ethylene production pathways.

2.3 Enviro-Economic Assessments

2.3.1 Process Modelling and Simulation

The foundation of environmental and economic assessments of chemical production routes are process models. These are a digital representation of the chemical process that calculates the mass and energy balances, and allows the sizing of the required equipment. These models are created using process simulator software, which are typically structured around three core modules: physical property models; flowsheet topology; and unit operation models (Haydary, 2019). Beyond this core structure, process simulators are split into two main types: sequential modular, and equation-oriented.

The sequential modular approach is the most common among process simulators, where each unit operation acts as an individual block within the flowsheet topology containing the necessary design and operating equations for that unit. The units are then connected together manually with material streams in a graphical user interface, and each unit is solved sequentially, where the outputs of one unit define the inputs of the next unit. This method is intuitive by nature, as the order of solving typically follows the flow of mass through the process, making errors easier to debug (Biegler et al., 1997). However, difficulties can arise when recycles are present, as multiple iterations are then required to achieve convergence. This can lead to a substantial increase in computational time, although most process simulators have convergence acceleration algorithms implemented to reduce the number of required iterations (Wegstein, 1958).

Equation-oriented simulators take a different approach, where all of the underlying mathematical equations describing the units and mass and energy balances are solved simultaneously. This significantly improves the capability to solve processes that have many recycles. Additionally, derivative information can be accessed via the underlying equations, which when coupled with efficient non-linear programming (NLP) solvers allows large models with over 100,000 equations to be solved (Dowling and Biegler, 2015). However, the disadvantage of equation-oriented simulators is that obtaining solutions can be heavily dependant on initial guesses, and when errors occur, they can be harder to

debug compared to sequential modular simulators (Pattison et al., 2017).

2.3.2 Techno-economic Analysis

Techno-economic analysis (TEA) is used to compare the economic performance of different technology options. It is based on calculating the capital and operating costs (CAPEX and OPEX respectively) of the process and using these to evaluate the overall economics. CAPEX consists of 4 main components when considering a chemical plant (Towler and Sinnott, 2022a):

- Inside Battery Limits (ISBL) i.e. the cost of the plant equipment itself
- Offsite Battery Limits (OSBL) i.e. the cost of adding or modifying the surrounding site infrastructure to accommodate the new plant
- Engineering and Construction
- Contingency

The ISBL forms the bulk of the CAPEX and is estimated using the purchased equipment costs as a foundation.

Purchased Equipment Cost

The main component of ISBL is the purchased equipment costs (or PEC) e.g the cost of the distillation columns, heat exchangers etc. Recent data should ideally be used to obtain accurate equipment costs, however this is commonly not readily available. As an alternative, cost correlations can be used to determine the purchased equipment costs of different types of equipment. For example, correlations proposed in (Towler and Sinnott, 2022a) take the following form:

$$C_e = a + bS^n \quad (2.6)$$

where C_e is the purchased equipment cost, a and b are cost parameters, S is the equipment size variable and n is the equipment exponent.

Note that correlation 2.6 gives the PEC in USD and assumes all of the equipment is made from carbon steel. If the equipment is made from other materials such as stainless steel, a linear material factor can be applied to the PEC to determine the new cost.

Factorial Method

Once the PEC has been determined, the CAPEX for the plant can be calculated by using the factorial method, which uses Lang factors (Lang, 1948). This method assumes that the ISBL of a plant is a linear function of the PEC and accounts for the installation, piping, electrical work etc. associated with the purchased equipment. The ISBL is calculated via the following equation (Towler and Sinnott, 2022a):

$$C_{ISBL} = F \sum C_e \quad (2.7)$$

Where C_{ISBL} is the ISBL cost and F is the associated Lang factor. Different values of F are used depending on the type of plant that is being built e.g. a fluid-based or solid-based plant. The factorial method can be expanded to include the OSBL, engineering and contingency costs to allow the total CAPEX to be obtained from just the PEC.

Cost Escalation

The correlation presented to calculate the PEC in the above section is in USD on a January 2010 basis. Therefore, the overall CAPEX calculated using the factorial method will also be in a January 2010 basis and must be adjusted to account for inflation and convert it to its present day value. Indices are available for each specific equipment type of the plant/process, but it is much simpler to use a weighted composite index for an overall chemical plant to adjust the costs. One of the indices that can be used is the Chemical Engineering Plant Cost Index (CEPCI), which is published every month by the Chemical Engineering journal (Chemical Engineering, 2022). To escalate the costs to the present day, the following equation is used:

$$C_{P,a} = C_{P,b} \frac{CEPCI_a}{CEPCI_b} \quad (2.8)$$

Where $C_{P,i}$ is the cost of the chemical plant in year i and $CEPCI_i$ is the index value in year i . The subscripts a and b represent the current year and reference year respectively.

Annualised Capital Charge

To evaluate the economic performance of a chemical plant, the CAPEX and OPEX must be considered together. Since the OPEX is typically given on a yearly basis, the CAPEX must be annualised over the lifetime of the plant. This annualisation of the CAPEX is known as the Annualised Capital Charge (ACC) (Towler and Sinnott, 2022a).

The ACC itself is calculated by considering the lifetime of the plant and the interest rate at which the initial investment must be repaid.

$$ACC = ACCR \times TCI \quad (2.9)$$

Where the TCI is the total capital investment of the plant and the $ACCR$ is the Annualised Capital Charge Ratio, which represents the fraction of the capital investment that must be paid back each year over the lifetime of the plant (Towler and Sinnott, 2022a):

$$ACCR = \frac{i(1+i)^n}{(1+i)^n - 1} \quad (2.10)$$

Where i is the interest rate and n is the lifetime of the plant. Once the ACC has been calculated, it is then combined with the OPEX to give the Total Annualised Cost of Production (TAC):

$$TAC = ACC + OPEX \quad (2.11)$$

This TAC can then be divided by the total amount of product produced by the plant to obtain the levelised cost of production of that product:

$$LCP = \frac{TAC}{F_P} \quad (2.12)$$

Levelised cost metrics are useful for comparing between different processes as they are scale-agnostic, unlike net present value methods. They also allow easier comparison with published market prices, which, although they are not the same as LCPs, can serve as a useful proxy for comparison to the current dominant technology.

2.3.3 Life Cycle Assessment

Life Cycle Assessment (LCA) is a methodological framework used to assess a product's or process's environmental impacts throughout all stages of its life cycle, which include raw material extraction, production/manufacturing, use and disposal (de Bruijn et al., 2002). The scope of an LCA over a product's entire life cycle is advantageous as it can reveal burden-shifting i.e. where detrimental effects are shifted either from one life cycle stage to another or between different environmental impacts (Finnveden et al., 2009). The methodology for LCA has been standardised by the International Organisation for Standardisation and consists of four main stages: goal and scope definition; inventory analysis; impact assessment; and interpretation (ISO, 2006).

The goal and scope definition stage is where the aims of the study are defined. This includes the definition of the study's functional unit, the system boundaries and the chosen allocation method. The choice of an appropriate functional unit is critical in an LCA to allow fair comparison between the options being assessed. The system boundaries for an LCA are typically defined as either cradle-to-gate or cradle-to-grave. The former considers impacts from raw material extraction up to the manufacture of a product before leaving the factory gate, and the latter includes the use phase and end-of-life treatment of the product. Allocation methods are also required in multi-product systems, where the impacts are either allocated on a mass or economic basis, or accounted for using a system expansion approach, where credits are given to the main product for avoiding the manufacture of the by-products by their typical route.

In inventory analysis, the required data is collected to perform the LCA study. A foreground inventory is created which consists of all inputs and outputs for the defined system with respect to the chosen functional unit. Background databases, such as the

ecoinvent database (Wernet et al., 2016), are used to connect the foreground inventory to background processes and allow the full system to be specified without gathering primary data all the way back through a supply chain to raw material extraction.

For impact assessment, the flows obtained from the inventory analysis stage are analysed to understand their environmental significance. This stage includes selection of impact categories; classification of the inventory data and characterisation of the inventory data. Impact categories can include global warming potential, land use and water consumption as examples. The inventory data is then assigned to the relevant impact categories and characterised into a total impact depending on a characterisation factor for the specific inventory flow.

Interpretation is the final stage, but is also performed continuously throughout the LCA. Here, the results from the inventory analysis and impact assessment are evaluated in order to generate a set of conclusions and recommendations for the assessed system/product.

In terms of software for performing LCAs, SimaPro is one of the most popular commercial offerings (PRé Sustainability, 2025), but there also open-source options which are gaining popularity, including both openLCA (Green Delta, 2025) and Brightway2, a Python-based LCA tool (Mutel, 2017).

2.4 Identified Gaps and Contributions

The review of literature in this chapter has revealed several research gaps that will be addressed throughout the remainder of this thesis. The first gap concerns the tools currently used to perform enviro-economic assessments of chemical processes. Currently, multiple tools and software are required to perform these assessments: a chemical process simulator, an economic assessment tool, and LCA software. However, these tools are disconnected, and performing an EEA can require a manually intensive workflow involving many “copy-paste” operations to move data between the software tools. Even if the chemical process simulator has built-in economic analysis, non-standard equipment must

still be defined, and if any changes are made in the underlying process simulation, the inventories for the LCA must be regenerated which can be very time consuming. From this, it is therefore worthwhile to explore options for a unified EEA framework that reduces the friction created by these disaggregated tools.

The second gap that emerges from the literature review is that whilst significant focus is placed on plastic waste as a circular feedstock, other feedstocks and conversion routes remain under-researched yet could still fill important roles in future circular ethylene production. Plastic will likely remain the primary feedstock choice for circular chemicals, but complementary sources and pathways will be needed to support the transition from a linear economy.

Three specific areas within this broader second gap warrant investigation, each representing distinct feedstock-to-ethylene pathways highlighted in the route map presented in Figure 2.5. First, municipal solid waste represents a feedstock that combines both plastic and biomass components, yet the enviro-economic trade-offs of MSW gasification for chemical production remain underexplored, particularly when considering different carbon management strategies (carbon capture and storage versus carbon capture and utilisation). Second, direct CO₂-to-ethanol synthesis offers a potential route that could integrate captured CO₂ with renewable H₂ to produce ethanol as an ethylene precursor, instead of the current state-of-the-art route via methanol synthesis. This could be preferable for cases where on-demand ethylene production is desired, instead of a light olefins mix as is produced via the MTO route. Third, if fuel-switching is performed in any chemical process where a methane by-product is combusted as a fuel source, that methane stream now represents a valorisation opportunity to manufacture additional chemicals. However, systematic evaluation of when chemical production from these streams offers greater value than combustion remains limited.

The contributions of this thesis in addressing these identified gaps are therefore as follows:

- **Chapter 3:** Development of a Python-based computational framework that unifies process simulation, techno-economic analysis, and life cycle assessment, eliminating

the manual data transfer workflows required by existing disaggregated tools.

- **Chapter 4:** Quantification of the enviro-economic performance of MSW gasification routes for methanol, ethanol, and olefins production, with explicit comparison of carbon capture and storage versus utilisation strategies against conventional waste management approaches.
- **Chapter 5:** Techno-economic analysis of a novel direct CO₂-to-ethanol process integrated within an ethylene value chain, determining its competitiveness against the established methanol-to-olefins pathway. Additionally, catalyst development targets are proposed to achieve further cost competitiveness.
- **Chapter 6:** Enviro-economic assessment of methane side-stream valorisation opportunities in fuel-switched chemical processes, establishing when chemical production from these streams offers greater value than continued combustion for heat.

Chapter 3

HysysPy: Streamlining enviro-economic assessments with Python

3.1 Motivation

As identified in Section 2.4, currently several disaggregated tools are required for performing enviro-economic assessments on chemical processes. Heavy copy–pasting workflows can be partially bypassed with Excel, with simulators such as those offered by Aspen-Tech integrating an "Excel Add-In" for exporting information. These types of add-ins are bi-directional, and can allow changes to be made to the simulation from Excel, opening up opportunities for running various scenario analyses that can be coupled with the techno-economic assessment. However, a link still has to be made to the LCA software, and any advanced analysis would likely require scripts to be written in Microsoft VBA.

With the rise in Python use within the chemical engineering field (Martín, 2020), its ability to interact with process simulators through the Windows COM interface (Santos Bartolome and Van Gerven, 2022), and the establishment of Brightway2 as a Python-based LCA software, the possibility to develop a Python package that can connect all three aspects of EEAs was identified. Aspen HYSYS was chosen as the chemical process

simulator that this package would be developed for as it is one of the most commonly used in both research and industry. Whilst there are already some packages published that interact with Aspen HYSYS through the Windows COM interface e.g. (Vázquez, 2025; Medina, 2025), none of these focus on enabling both TEAs and LCAs of the underlying chemical process model. From this gap, a Python package called HysysPy was developed as the foundation for performing EEAs in this thesis, with the overall aim of streamlining EEAs for chemical processes.

3.2 Overview

The HysysPy package provides a unified Python interface for performing enviro-economic assessments on chemical processes modelled in Aspen HYSYS. It bridges process simulation, techno-economic analysis, and life cycle assessment within a single programmatic workflow, eliminating the need for manual data transfer between disparate software tools.

Figure 3.1 illustrates the overall architecture of HysysPy and its relationship with Aspen HYSYS. The package establishes a connection to an open HYSYS flowsheet through the Windows COM interface, enabling bidirectional communication. Through this connection, HysysPy can read stream and equipment data, modify operating parameters, and perform flowsheet recalculations programmatically.

The package comprises four interconnected modules that transform raw simulation data into comprehensive enviro-economic metrics. The **equipment sizing** module automatically identifies and sizes standard unit operations within the flowsheet, such as pumps, compressors, and distillation columns. These sized-units then feed directly into the **techno-economic analysis** module, which applies cost correlations and factorial cost estimation methods to determine capital expenditure.

Simultaneously, the **heat exchange network** module performs pinch analysis on the flowsheet's streams to identify opportunities for heat integration. This module calculates minimum utility requirements and estimates network area, with the resulting duty and fuel consumption data flowing into both the economic analysis (as operating expenditure)

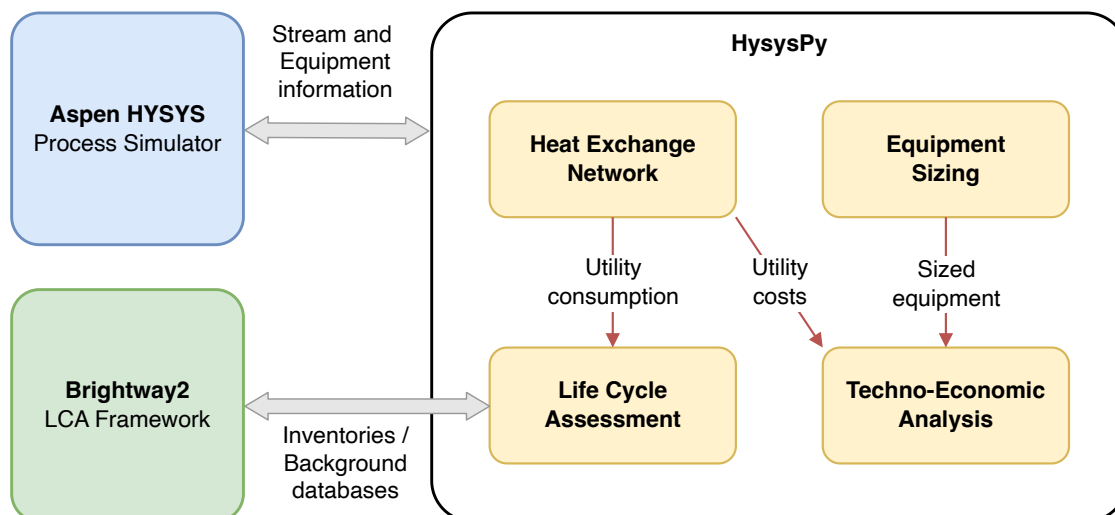


Figure 3.1: Architecture of the HysysPy package and its relationship with Aspen HYSYS and Brightway2.

and the environmental assessment.

Finally, the **life cycle assessment** module constructs a life cycle inventory from the flowsheet’s material and energy flows. It interfaces with the Brightway2 framework to link foreground process data with background databases, enabling characterisation of environmental impacts across multiple assessment methods.

This modular architecture ensures that any changes made to the underlying HYSYS flowsheet propagate automatically through all assessment calculations, facilitating rapid iteration and scenario analysis. The following case study demonstrates these capabilities through a practical example, though the same workflow applies to any chemical process modelled in Aspen HYSYS.

3.3 Case Study: Sustainable Ethylene on Teesside

3.3.1 Context

A collaboration with the North East of England Process Industry Cluster (NEPIC) offered an opportunity to test the capabilities of HysysPy. Ensus, one of NEPIC’s members, are a manufacturer based on the Teesside chemical cluster and manufacture bioethanol made

from wheat fermentation. Their plant produces over 400 million litres of ethanol per year and their main end-use for ethanol is the E10 petrol used throughout the UK (Ensus, 2025). However, with future government policy aiming to ban the sale of combustion engine cars in the UK by 2030 (Department for Transport, 2025), Ensus were interested in alternative markets for their ethanol.

One of these potential other markets is ethylene production via ethanol dehydration, as introduced in Section 2.1.2. The goal of the case study was to therefore perform an EEA on ethanol dehydration to produce ethylene.

3.3.2 Model Description

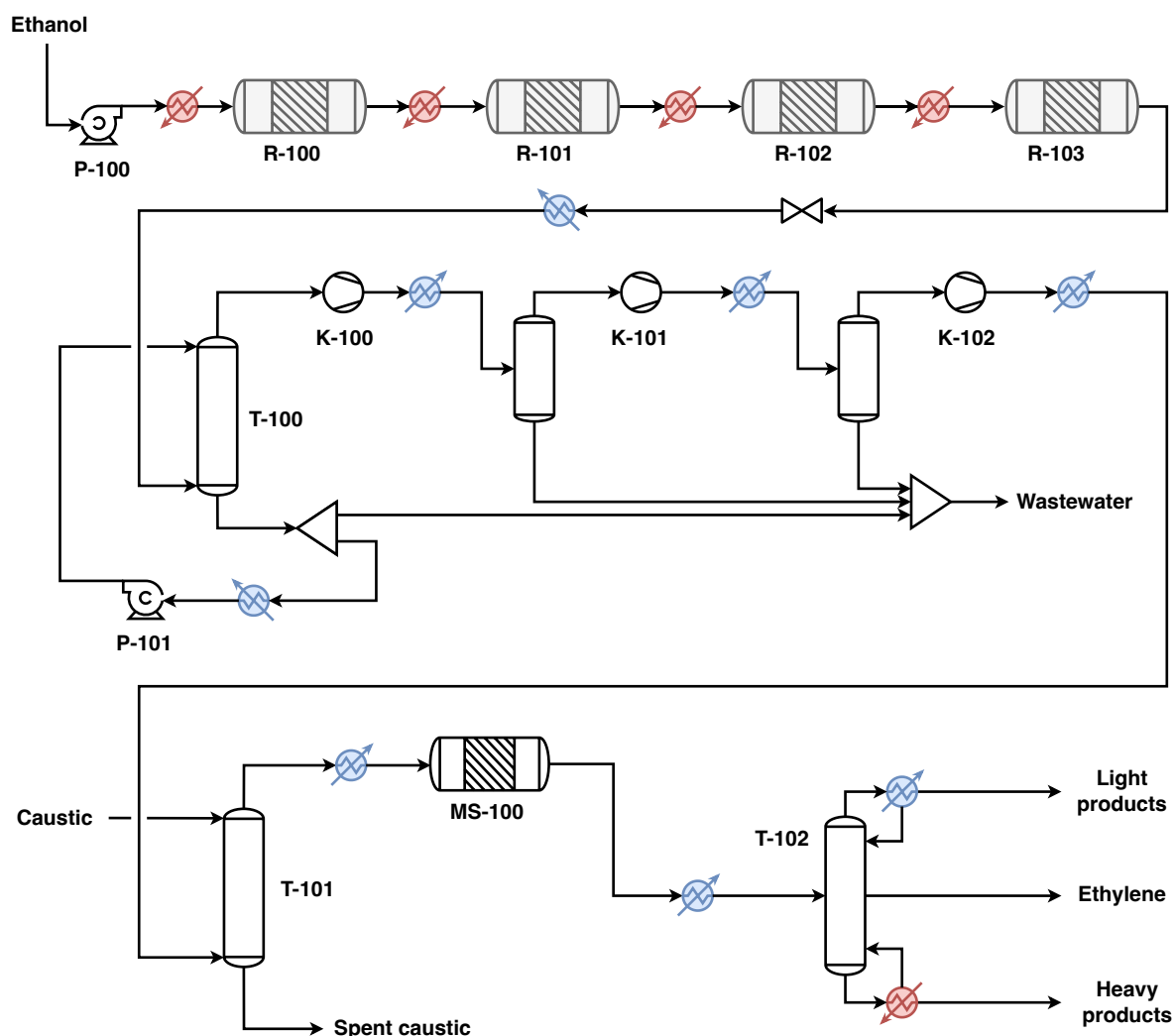
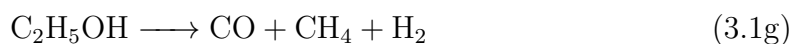
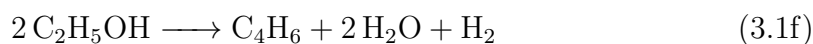
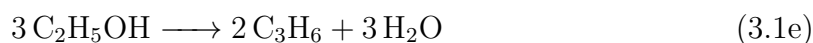
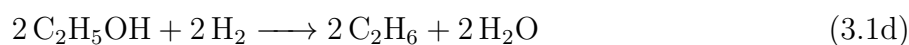
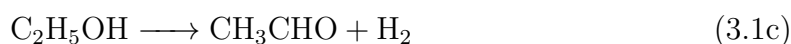
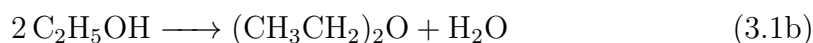
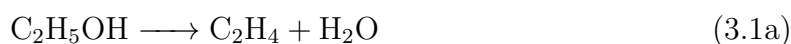


Figure 3.2: Process flow diagram for ethanol dehydration to ethylene.

The ethanol dehydration to ethylene (ETE) model for this case study is based on the work by Mohsenzadeh et al. (2017) and is summarised in Figure 3.2. The process is split into three main sections: the reaction, purification, and recovery sections. First, ethanol is fed to the reaction section and pumped to 11.4 bar and heated up to 450 °C. The ethanol is then fed into a series of four packed bed adiabatic reactors (R-100 to R-103) filled with a γ -alumina catalyst. In HYSYS, this is modelled as four conversion reactors with eight parallel reactions that produce the main product, ethylene, along with other by-products including ethane, 1,3-butadiene, diethyl ether, propylene, acetaldehyde, hydrogen and methane. The eight reactions modelled in this work are shown below, with selectivities taken from Arvidsson and Lundin (2011):



Due to the highly endothermic nature of ethanol dehydration, reheating up to 450 °C is required after each reactor bed. Across the four reactors, the total ethanol conversion reaches 99.5%, and the ethylene selectivity reaches 98.8%.

After the reaction section, the product mixture is cooled and flashed down to 95 °C and 2 bar, respectively, and fed to the purification section. The mixture is sent to a water quench tower (T-100), where the product stream is cooled further and approximately 90% of the produced water from the reaction section is removed. Note that the condensed water is recirculated after passing through a 10% purge to remove the need for external water consumption during steady state operation. The gaseous stream leaving the water

quench tower consists primarily of ethylene (88mol%), some remaining water (10mol%), unreacted ethanol (0.5mol%) and other by-products. The stream is compressed in a multistage compression train (K-100 to K-102) with intercooling to reach 27 bar. Condensed water is removed at each stage in a flash vessel, along with the small quantity of unreacted ethanol. After compression, any CO₂ remaining in the product mixture is removed in a caustic wash column (T-101) fed with 10 wt% NaOH solution. This reduces the concentration of CO₂ in the stream from approximately 1600 ppm down to less than 1 ppm, which meets the purity requirements for polymer grade ethylene. The final stage of purification is passing through a molecular sieve dryer (MS-100) to remove all final traces of water (GPSA, 2016).

In the recovery section, the predominantly ethylene product stream is cooled down to -18 °C and sent to a cryogenic distillation column (T-102). Here, the heavy by-products (ethane, propylene, 1,3-butadiene, diethyl ether) are removed from the bottom of the column, and the light impurities (mainly hydrogen and methane) are removed from the top of the column. Both of these side-product streams are combusted to help close the overall energy balance of the plant. The ethylene product is removed via a side draw near the top of the column with a 99.98 mol% purity, which meets the required purity specification for polymer grade ethylene.

3.3.3 HysysPy Setup and Equipment Sizing

After importing the HysysPy module, and ensuring that the desired HYSYS flowsheet is open, creating an instance of the HysysPy class will initialize the desired COM connection:

```
from hysyspy import HysysPy  
model = HysysPy()
```

At a high level, materials streams and unit operations can be accessed from the HysysPy model through the names as given in the HYSYS flowsheet, and then their attributes can also be accessed and adjusted:

```
stream = model.MaterialStreams("<STREAM_NAME>")
stream.TemperatureValue = 100
```

HysysPy can search through a flowsheet to gather and size standard chemical process equipment without additional setup:

```
model.get_equipment()
```

The list of standard equipment automatically covered include:

- Compressors
- Expanders/Turbines
- Pumps
- Flash vessels
- Three phase separators
- Packed absorbers
- Trayed distillation columns
- Packed bed reactors

Additionally, if specialised equipment is present, a custom Equipment class can be defined that inherits from one of the Equipment classes used in HysysPy. At a minimum, this needs to define a calculation for the size parameter for the equipment, as well as the parameters a , b , and n used by the cost curve correlation in the form $a + bS^n$. Additionally, the CEPCI should be specified and the ISBL installation factor for the factorial method if applicable. Below shows an example of how this can be set up, where `op` is the object from HYSYS:

```
from hysyspy import Equipment

class CustomEquipment(Equipment):
    def __init__(self, op):
        super().__init__(op, a=100, b=200, n=0.7,
                        isbl_factor=2, cepci=600)

        # define custom sizing calculations
        self.size = self.calculate_size()
```

Since conversion reactors were used in the reaction section for the ETE model, a custom `DehydrationReactor` class was defined to size and cost them. This inherited the calculation methodology from HysysPy's `PFR` class, which calculates the cost of a PFR based on the unit's volume and pressure, from which the shell thickness is inferred (Towler and Sinnott, 2022a). The `PFR` class (and other available equipment types) all inherit from the same master `Equipment` class for costing as introduced above; the only difference is the methodology used to determine the size parameter. Please see A for the implementation of the `DehydrationReactor` class in Python. Once defined, the custom equipment can then be added to the model's equipment list after linking it to the `Operation` object defined in HYSYS:

```
reactor_operation = model.Operations("<HYSYS_REACTOR_NAME>")
reactor_python = DehydrationReactor(reactor_operation)
model.add_equipment(reactor_python)
```

This was repeated for each of the four dehydration reactors.

3.3.4 Heat Exchange Network

HysysPy can also use pinch analysis to determine the minimum heating and cooling requirements after heat integration for a given minimum approach temperature, `tmin`. This is achieved by first extracting the heat exchanger stream information and calculating the hot and cold stream heat transfer coefficients. Utilities are provided which match those available by default in Aspen HYSYS (i.e. fired heat, steam at low, medium, and high pressure, cooling water, and various levels of refrigeration down to -160°C). Next, an MILP is defined in Pyomo (Bynum et al., 2021) that describes the heat balance across the temperature intervals in the heat exchange network (Smith, 2005). Furthermore, it can also estimate the area of the heat exchange network using the Bath formula, which assumes vertical matching on enthalpy intervals between the hot and cold composite curves (Smith, 2005).

```
model.size_hen(tmin=10, area_method='bath')
```

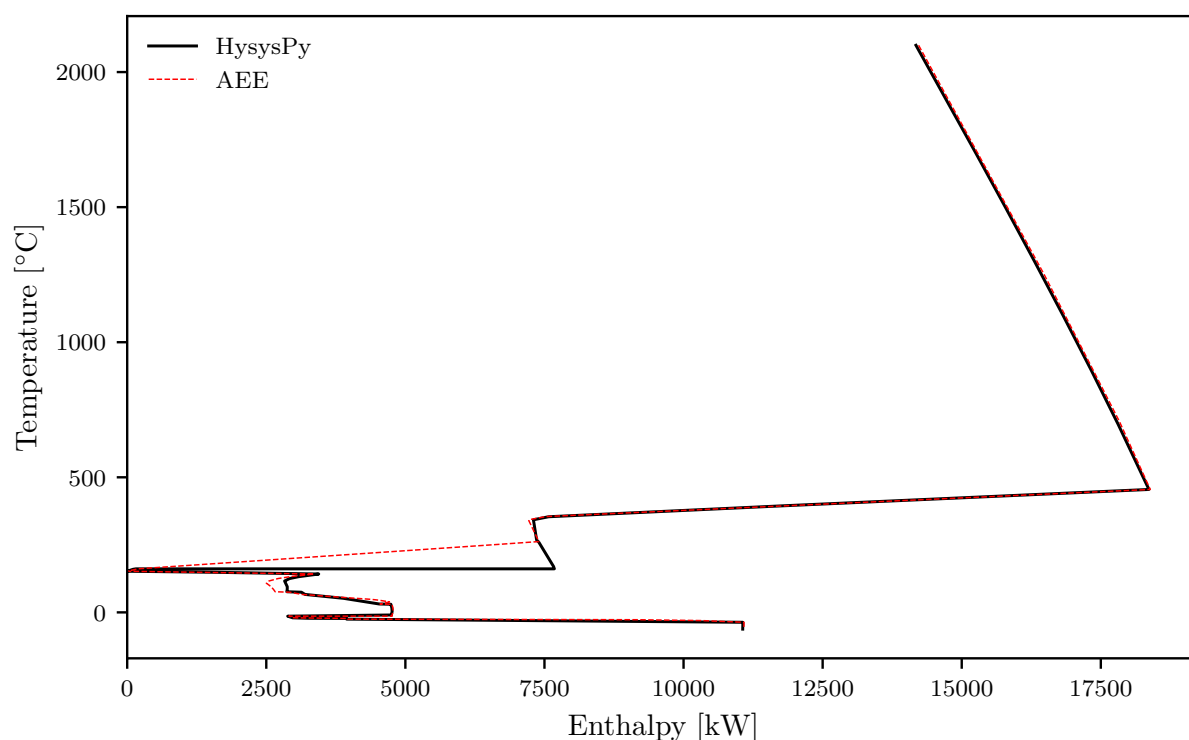


Figure 3.3: Grand composite curve from HysysPy compared with Aspen Energy Analyzer.

Figure 3.3 shows the resulting grand composite curve (GCC) obtained for the ETE process, which also illustrates a strong match with the majority of the GCC obtained using Aspen Energy Analyzer (AEE). Note that the high upper temperature in the GCC comes from the modelling of the combustion of the light and heavy by-products, which were cooled to provide additional heating for the process. The cause for the large discrepancy at approximately 250°C is the different segmentation procedures used by AEE and HysysPy to calculate the physical properties for the streams within the heat exchangers, and these differences are exacerbated in heat exchangers with phase changes.

Further to this, Table 3.1 compares various heat exchange network metrics between HysysPy and Aspen Energy Analyzer. Whilst the minimum utility duties, pinch temperature and minimum number of units show excellent agreement, differences arise in the estimated area due to the aforementioned differences in segmentation. This changes the calculated physical properties, and therefore heat transfer coefficients within each enthalpy interval, which changes the estimated heat exchange area.

Table 3.1: Comparison of HEN metrics from HysysPy and Aspen Energy Analyzer.

Metric	HysysPy	AEE	Deviation [%]
Minimum heating [kW]	14177	14224	0.3
Minimum cooling [kW]	11063	11084	0.2
Pinch temperature [°C]	152.3	152.3	0.0
Minimum number of units [-]	25	25	0.0
Estimated area [m ²]	11742	13804	17.6

Under development currently is the ability to calculate the HEN area using the sequential method described by Biegler et al. (1997). Whilst this is more accurate than the Bath formula method currently implemented, it is significantly more computationally demanding, especially for solving the MILP transshipment subproblem for determining the minimum number of matches due to its combinatorial nature (Chen et al., 2015). Additionally, after the capital cost of a HEN is annualised along with the rest of the equipment, it becomes a smaller proportion of the overall TAC, and therefore the gains in accuracy typically have little effect on the final result (Gonzalez-Garay and Guillen-Gosalbez, 2018). Future work could also implement the simultaneous method of HEN

design proposed by Yee and Grossmann (1990), which involves solving an MINLP model describing a stage-wise superstructure representation of the network.

3.3.5 Techno-Economic Analysis

After all the equipment has been defined and sized, and the HEN designed, the CAPEX can be automatically calculated using the built-in cost curves for each equipment type, then using the factorial method introduced in Section 2.3.2 to determine the TCI. For the operating costs, the streams must be added by providing the stream name as defined in HYSYS, the stream type, and the stream's unitary cost in USD per kg. Additionally, if only a specific component in a stream needs to be added for economic or environmental purposes e.g. CO₂ emissions in a generic flue gas stream, then the component name can also be specified to only account for the mass flowrate of that specific component. Note that the stream type can either be a product, raw material, or a waste stream.

```
model.add_stream(  
    stream_name="<STREAM_NAME>",  
    stream_type="<STREAM_TYPE>",  
    component="<COMPONENT_NAME>",  
    cost=<COST>,  
)
```

This is repeated until all relevant streams have been added to the HysysPy object. Once all of the streams have been added, the TEA for the model can be initialised with some additional economic parameters:

```
model.calc_tea(  
    cepci=796.2, # CEPCI 2024  
    n=20, # lifetime of plant in years  
    i=0.1, # 10% interest  
    plant_type="f", # fluids processing plant
```

```
elec_cost=0.1, # usd/kwh  
fuel_cost=0.05, # usd/kwh  
hours=8000, # hours per year operation  
)
```

This performs a full TEA on the given HysysPy model, including calculation of the ACC using the purchased equipment costs of the sized HYSYS equipment, determination of the variable and fixed operating costs, and the final calculation of the TAC. Each of the main economic results can be accessed through attributes in the calculated TEA object, for example, the TCI and VCP are both accessed through:

```
TCI = model.tea.capex.tci  
VCP = model.tea.opex.vcp
```

For the ethanol dehydration case study, the average cost of electricity, natural gas, and ethanol over the 2018-2024 year period were used for the economic analysis (Trading Economics, 2025). Figure 3.4 displays the obtained equipment cost (and therefore total CAPEX) breakdown, as well as the operating cost breakdown.

The key finding from Figure 3.4 is that over 90% of the operating costs are due to raw materials, specifically the ethanol feedstock. Exploring this further, again using the results accessible from HysysPy, the levelised cost of production (LCP) of bioethylene (BIO) is compared to the average 2022 market price of ethylene produced from steam cracking i.e. the business-as-usual (BAU) route (STATISTA) in Figure 3.5.

The cost of bioethylene is only 5% more expensive than the BAU route, at 1.31 USD/kg versus 1.25 USD/kg, respectively. It is also clear that the ethanol feedstock costs dominate the overall cost of bioethylene, at 86% of the total LCP. This implies that if cheap ethanol can be sourced, then there is potential for ETE to become competitive with steam cracking.

To explore this further with a more in-depth market scenario analysis, HysysPy enables easy updating of stream prices once the base TEA has been created:

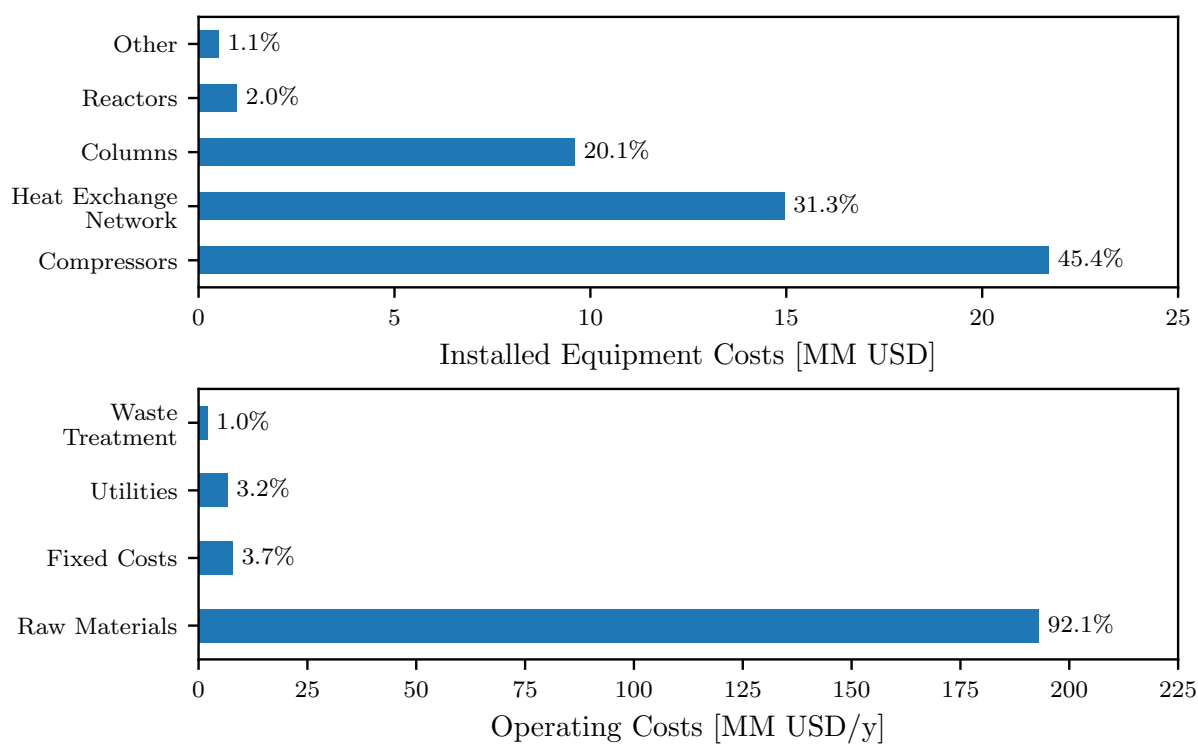


Figure 3.4: Equipment cost and OPEX breakdown

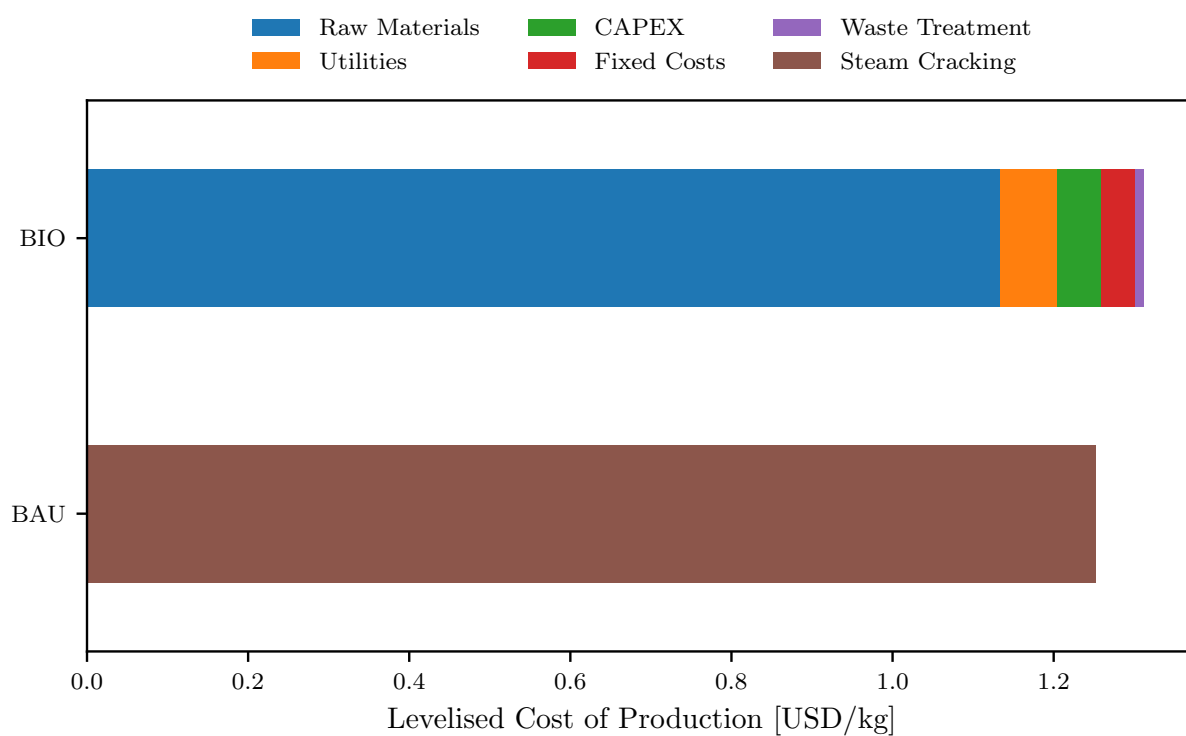


Figure 3.5: Levelised cost of production of ethylene comparison

```
model.tea.update_prices({"<STREAM_NAME_1>": <NEW_PRICE_1>})
```

The relevant economic attributes are then automatically recalculated. This can be utilised to evaluate the LCP of bioethylene across the whole 2018-2024 period, using weekly prices of ethanol, electricity and natural gas as the heating source.



Figure 3.6: Variation in costs of production for ethylene via BIO and BAU routes from 2018-2024, and the relative price between them.

Figure 3.6 shows the variation in bioethylene's LCP compared to the market price of ethylene from steam cracking. To the right of the figure is also the relative price (RP) between the two options:

$$RP = \frac{LCP_{BIO}}{LCP_{BAU}} \quad (3.2)$$

From 2018-2020, the BIO route was actually cheaper than the BAU route, thanks to cheap ethanol in this period (less than 1.5 USD/gal). After the COVID-19 pandemic in 2020, the BIO route has been more expensive on average, but considering the distribution of RPs throughout the whole six year period reveals that the median BIO LCP is only 2% more expensive than the BAU route. Furthermore, 75% of market scenarios result in a BIO price that is under 1.5 times that of the BAU route, indicating that ethanol dehydration can be competitive with steam cracking, assuming ethanol can be sourced

cheaply.

3.3.6 Life Cycle Assessment

HysysPy can create life cycle inventories based on the connected Aspen HYSYS flowsheet, which can subsequently be used to create activities in Brightway2 for life cycle assessment. A prerequisite to using HysysPy is setting up the relevant project and databases in Brightway2. Once that is done, an LCA object can be initialised by passing in the name of the Brightway2 project, the streams saved in the model, the name of the stream that will act as the functional unit (for this work, this is the ethylene product stream), a given name for the process/activity that will be created in Brightway2, and finally the utilities and electricity usage calculated by the HEN and TEA modules earlier:

```
from hysyspy import LCA

lca = LCA(
    project_name="<BW2_PROJECT_NAME>",
    functional_unit="<STREAM_NAME>",
    process_name="<PROCESS_NAME>",
    streams=model.streams,
    electricity=model.tea.opex.total_elecectricity,
    utilities=model.hen.utilities,
)
```

Afterwards, the streams need to be linked to a specific activity in the background database to perform the calculation. HysysPy simplifies this by providing a keyword search functionality. For example, the following connects the ethanol feed stream to 95% ethanol production from rye fermentation in Europe (or RER), which is the closest activity to wheat fermentation in the ecoinvent 3.10 database.

```
lca.add_stream_data(  
    stream_name="ethanol_feed",  
    search_terms={  
        "name": ["ethanol", "rye"],  
        "location": ["RER"],  
        "reference product": ["ethanol", "95%"],  
    },  
    lca_conversion_factor=1,  
)
```

It also allows any conversion factor to be provided in case the background activity unit is not in kg. This is repeated for each stream, as well as the electricity and fuel used in the process. Note that the electricity and fuel requirements are calculated for each of the utilities defined by the HEN, so linking electricity and fuel to the background database covers all of the utilities. Once all the streams and utilities have been linked to the background database, the foreground life cycle inventory and activity are created in the Brightway2 project:

```
lca.create_activity(  
    location="GB",  
    code="ensus",  
    unit="kilogram",  
)
```

This normalises all of the stream flowrates and utilities with respect to the functional unit stream. After this, the newly created activity can be used as normal within Brightway2 to perform a life cycle assessment.

For the goal and scope of this case study's LCA, the functional unit was chosen to be 1 kg of ethylene and the assessment was made on a cradle-to-gate basis. Note that since the ethanol is sourced from biomass in the BIO route, a credit is given to account for the

sequestration of biogenic carbon within the ethylene product molecule. The ecoinvent 3.10 database was used for the background inventories (Wernet et al., 2016), and the ReCiPe 2016 method was used to assess the midpoint global warming potential (GWP), and the three endpoint impacts (damage to human health, damage to ecosystem quality, and resource depletion) (Huijbregts et al., 2017). A naphtha steam cracking process is also taken from ecoinvent to represent the BAU route, which was then compared to the BIO route.

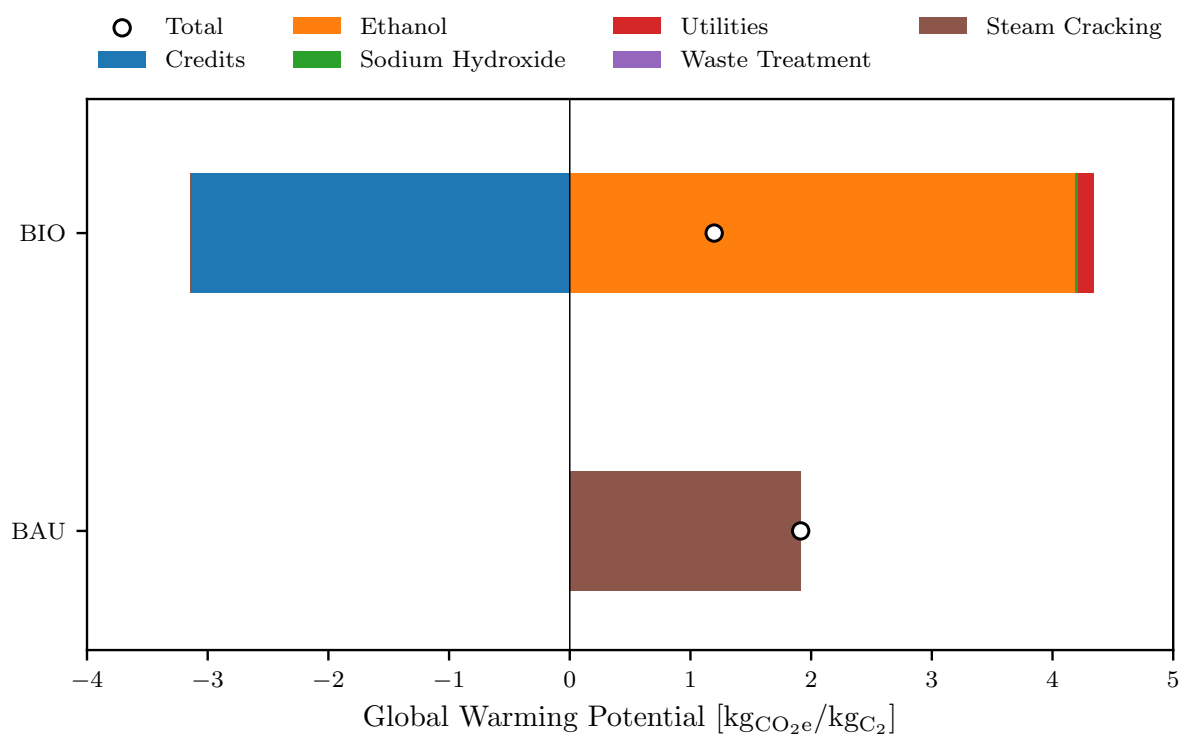


Figure 3.7: Global warming potential of bio-ethylene versus business-as-usual (BAU) steam cracking.

Figure 3.7 shows the obtained results for the GWP of the two routes. Overall, the GWP of the BIO route is lower overall compared to the BAU route at 1.20kgCO_{2e} versus 1.91kgCO_{2e}, respectively. However, this is mainly due to the large biogenic CO₂ sequestration credits equalling 3.1kgCO_{2e}, which offsets most of the 4.2kgCO_{2e} of emissions from the ethanol feedstock. This is primarily from agriculture emissions from growing the rye to produce the ethanol, as fertiliser production and their subsequent breakdown in soil lead to significant emissions (Gao and Cabrera Serrenho, 2023).

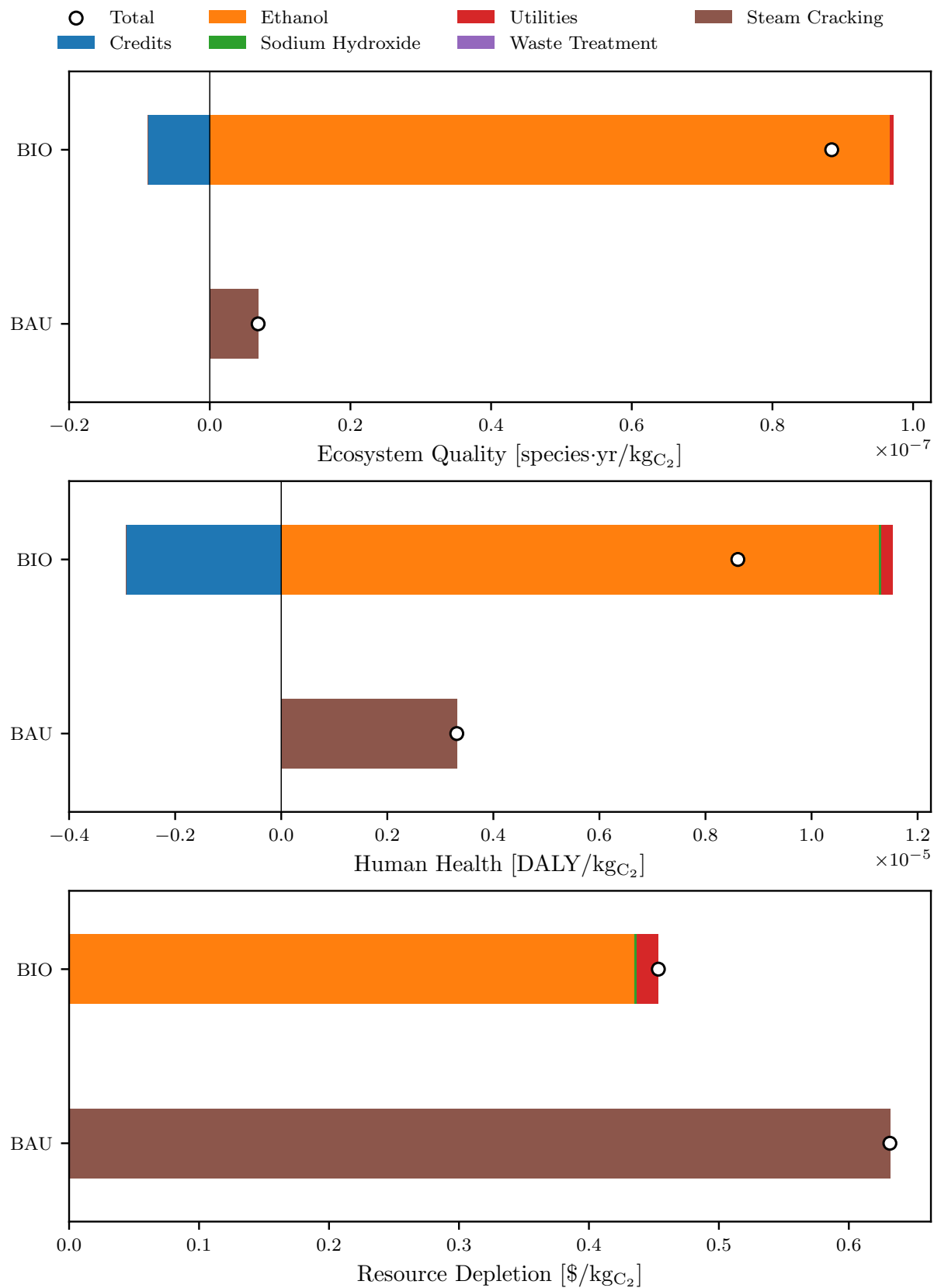


Figure 3.8: Endpoint impacts of bio-ethylene versus business-as-usual (BAU) steam cracking.

Figure 3.8 shows the obtained LCA results for the three endpoint impacts. For both ecosystem quality and human health impacts, the BIO route creates significantly more damage than the BAU route, at 12.8 times greater for ecosystem quality, and 2.6 times greater for human health. When damage is aggregated to these endpoint impacts, the credits for sequestering CO₂ in the BIO route are not enough to offset the environmental impacts of agriculture in other midpoint areas (e.g. land use, water consumption, terrestrial ecotoxicity etc.). There is a reduction in impacts for resource depletion, with the BIO route 28% lower than the BAU route, as the fossil resources required for growing the rye are still less than what is required to produce ethylene from fossil-based naphtha. These results emphasise the care that must be taken when assessing a “greener” process that uses biomass as a feedstock. When the broader environmental impacts are considered, it may potentially be more damaging than the current fossil-fuel based route. Note, however, that these results are sensitive to the choice of biomass feedstock for producing the ethanol, as there are large variations in impacts depending on the type of biomass and the region where they are grown (Shakelly et al., 2023; Soleymani Angili et al., 2021). However, a comparative assessment between different feedstocks is beyond the scope of this case study illustrating the capabilities of HysysPy.

3.3.7 Other Capabilities

Interacting with Aspen HYSYS through Python also unlocks many useful capabilities beyond performing EEAs through HysysPy, including linking the flowsheet to black-box optimisation solvers, and performing sampling for either sensitivity analysis or generating training data for surrogate models (Triantafyllou et al., 2024). For these cases where large samples must be gathered from a flowsheet, HysysPy can also enable parallel evaluation of HYSYS flowsheets to reduce the computation time. If the computer being used for analysis has enough RAM and a powerful enough CPU, multiple instances of HYSYS can be run at once. If the filenames have a unique identifier (e.g. `ethanol_dehydration_1.hsc`, `ethanol_dehydration_2.hsc` etc.), then HysysPy can be used to connect to a specific instance:

```
model1 = HysysPy(instance='1')  
model2 = HysysPy(instance='2')
```

Whilst this capability wasn't directly used in this thesis, it expands the usefulness of HysysPy as a tool for other users working with Aspen HYSYS flowsheets.

3.4 Conclusions

This chapter introduced HysysPy, a Python package developed with the aim of streamlining EEAs in Aspen HYSYS. By connecting directly to the HYSYS flowsheet object, integrating equipment sizing and economic analysis, and creating life cycle inventories and activities for use within Brightway2 for LCA, the time to perform and iterate EEAs is significantly reduced. This time reduction also opens up the possibilities of more thorough economic and/or environmental analyses, as changes made in the flowsheet can be automatically propagated throughout the required assessment.

The capabilities of HysysPy were demonstrated through a simple case study investigating the enviro-economic performance of bioethylene production via ethanol dehydration from wheat fermentation. Whilst economically, the bioethylene route can be very competitive with steam cracking, especially in periods with low ethanol prices, the environmental impacts are significantly greater in two of the three endpoint impact categories. This highlights the importance of considering burden shifting when analysing an apparently more sustainable option, as well as the high environmental impacts of the agriculture sector.

To conclude, HysysPy enables streamlined EEAs to be performed on chemical processes, and forms the foundation for the analysis presented in the subsequent chapters.

Chapter 4

Municipal Solid Waste Gasification

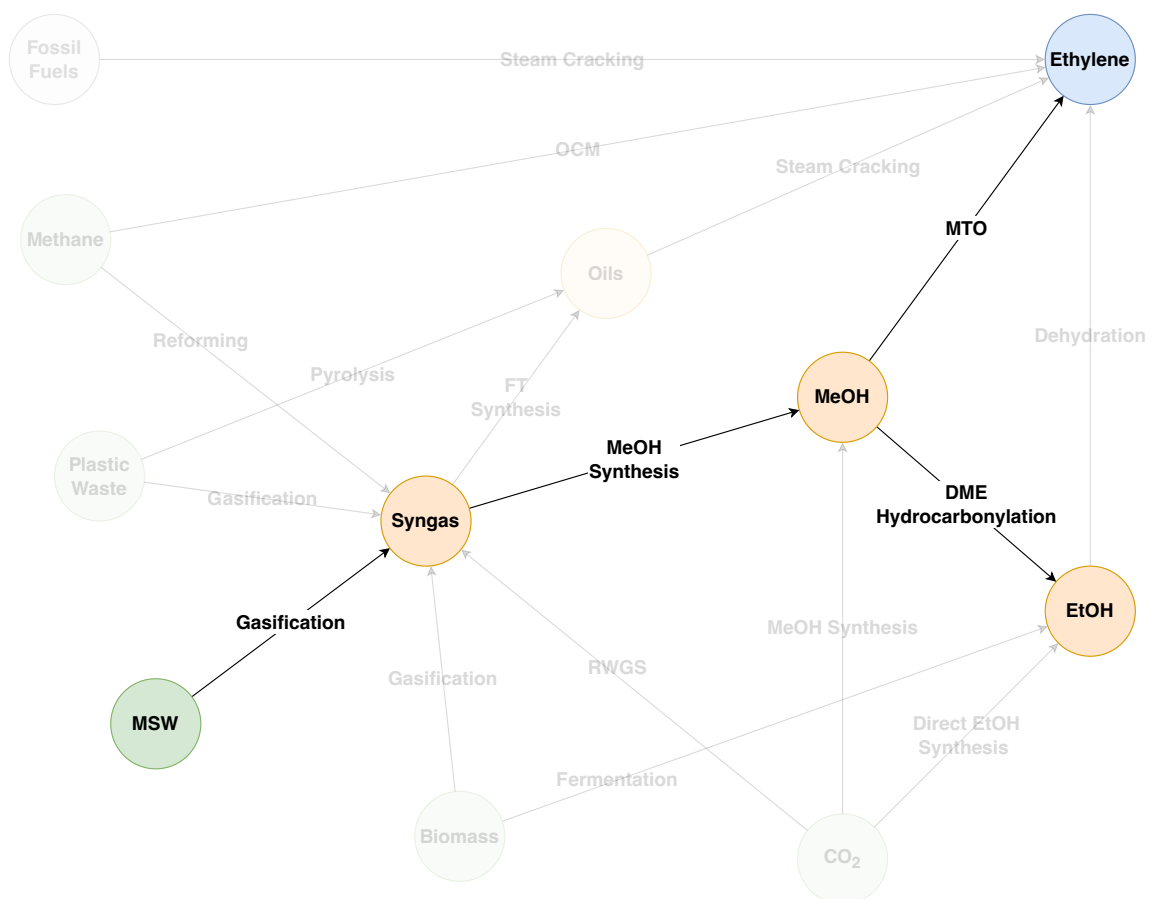


Figure 4.1: Overview of production routes assessed in Chapter 4.

4.1 Introduction

The generation and inadequate disposal of municipal solid waste (MSW) is a serious threat to the future and sustainability of the planet. An ever-increasing population coupled with improvements in standards of living, higher levels of urbanisation and economic development all contribute to the increasing rate of waste generation (Kumar and Samadder, 2017). In 2016, it was estimated that over 2 billion tonnes of waste was generated globally, predicted to rise to over 3.4 billion tonnes by 2050 (Kaza et al., 2018). Currently, over two thirds of this waste is disposed of in an uncontrolled manner; either through open dumping or landfilling. This improper waste management leads to both significant health risks to local populations, and damage to ecosystems, as material and leachate can leak into the surroundings. On top of damaging compounds entering the environment, uncontrolled dumping and landfilling results in over 1.6 billion tonnes of CO₂ emissions every year. This equates to 5% of global CO₂ emissions, and, with the predicted waste increase, will rise to 2.6 billion tonnes in 2050 (Kaza et al., 2018). Looking at the UK specifically, over 29 million tonnes of MSW is generated annually, which corresponds to 18.2 million tonnes of CO₂, or 5% of the country’s total annual CO₂ emissions (Office for National Statistics (UK), 2024b; OECD, 2024; Tolvik Consulting, 2024; Office for National Statistics (UK), 2024a). It is clear then that the need for appropriate waste management solutions is crucial for the future of the planet and humanity.

Various technologies are being researched and implemented in order to improve the sustainability of waste management systems. One such technology is incineration, which is increasingly being used in developed countries in an attempt to reduce the impacts of landfilling. The main advantage of incineration is the significant reduction in both mass and volume of waste that is destined for landfill (~80–90% reduction), and in turn, the land use required for those landfills (Arena, 2012). Incineration also helps to move away from the purely linear economy model (i.e. “extract-produce-use-dump”) in landfilling systems, and towards a more circular economy via the net generation of both electricity and heat from MSW. Nevertheless, a core component of a circular economy is narrowing and closing material and energy loops as much as possible (Geissdoerfer et al., 2017).

MSW incineration can be considered a long outer loop in that respect, as only fraction of the embedded energy is recovered and any material value is lost (Ellen Macarthur Foundation, 2013). Additionally, since MSW incineration falls under the *recovery* level in the EU waste hierarchy (Malinauskaite et al., 2017; European Commission, 2017), it should not hinder the implementation of systems and technologies that could promote the upper levels in the waste hierarchy (prevention, re-use and recycling) and enable a more sustainable circular economy (Korhonen et al., 2018; Ellen Macarthur Foundation, 2019b).

An alternative waste management solution to incineration that is garnering increased interest in both research and industry is gasification, where the waste feedstock is partially oxidised using various gasifying agents, such as steam, air and/or oxygen. This yields syngas, a mixture composed of CO, H₂, CO₂, CH₄, and other compounds such as tars, ashes, etc. Like incineration, electricity can still be generated by combusting the syngas in a turbine, but also, with sufficient cleaning, the syngas can be used as a feedstock for fuel and chemical synthesis (Arena, 2012). Whilst a lot of research has focused on gasification in waste-to-energy applications (e.g., Di Gregorio and Zaccariello, 2012; Dong et al., 2018; Lee, 2022; Arena et al., 2015; Lombardi et al., 2015; Ouedraogo et al., 2021), its use in chemical manufacturing is increasingly looking attractive as it presents itself as a chemical recycling technology. Compared to incineration, this approach falls under the *recycling* level of the EU waste hierarchy, and subsequently presents a smaller material/energy loop (Iaquaniello et al., 2018; Voss et al., 2021). As a potential chemical recycling technology, gasification has other advantages as well. Not only is the waste feedstock abundant and available throughout the year, but there is also an economic incentive as the feedstock can be a source of revenue through a gate fee (Aracil et al., 2017). Furthermore, there is no competition for the waste as a feedstock for other processes, as is the case in the “Food vs. Fuel” debate surrounding crop usage for bio-fuel production (Tenenbaum, 2008).

There have already been various studies on chemical manufacture from MSW gasification. (Niziolek et al., 2015a) used a mixed-integer nonlinear optimisation (MINLP) model to determine that methanol and Fischer-Tropsch fuels produced via MSW gasi-

fication plants could achieve production costs as low as \$61/barrel with an appropriate gate fee for the waste. (Sun and Tang, 2023) further explored fuel production via MSW gasification, comparing methane, methanol and DME production and identified trade-offs between the routes in various metrics, such as exergy efficiency (61% for methane), CO₂ intensity (1.57 kg/h per tonne of methanol produced), and net-present value (\$770/tonne for DME). (Ostadi et al., 2023) highlighted the importance of H₂ supplementation in MSW gasification for chemical production, as the carbon efficiency of methanol synthesis could be increased from 44% to 94%. However, recent work from (Voss et al., 2024) revealed that MSW gasification routes were significantly more expensive than landfilling, and had much higher capital investments compared to incineration.

Even though gasification routes appear to be more expensive, the literature offers support that they are a more sustainable waste management solution. In the same work, (Voss et al., 2024) also found that the gasification routes had the lowest global warming potential (GWP), and could be net-negative. (Nuss et al., 2013) reported that ethylene production via MSW gasification offers lower environmental impacts (such as GWP, energy demand, acidification) compared to landfilling, but it would only be cost competitive with fossil production with high gate fees. (Keller et al., 2020) estimated that a 72% reduction in GWP could be obtained with olefins manufactured via MSW gasification compared to the standard naphtha-cracking based routes. (Castagnoli et al., 2024) also identified the importance of H₂ supplementation in MSW gasification from an environmental perspective, as methanol synthesis with additional H₂ reduced GWP by 66% compared to incineration. Without this supplementation, the methanol yield was halved, and thus significantly reduced the avoided methanol production emissions and increased the GWP.

To the best of the authors knowledge, there has not been any research on the cost of externalities arising from environmental impacts for chemical manufacture via MSW gasification. This is important in order to obtain a full picture of the environmental damage that these MSW gasification routes may cause, or the potential savings when coupled with chemical synthesis. Therefore, in this chapter, the economic and environmental per-

formance of three chemical manufacturing routes coupled with MSW gasification will be assessed. These three routes are: i) methanol synthesis; ii) ethanol synthesis via DME hydrocarbonylation; and iii) ethylene and propylene synthesis via methanol-to-olefins. Two variations of these routes will be assessed to investigate the trade-off between H_2 supplementation and CO_2 removal: one with CO_2 recycling and additional H_2 (CCU); and another with CO_2 removal and storage (CCS). The gate fees for the gasification routes are determined and compared to those of landfilling and incineration facilities. Furthermore, an LCA compares the gasification routes to landfilling and incineration, with the computation of both midpoint and endpoint environmental indicators. Finally, the environmental externalities of the gasification routes will be monetised and added to the gate fee in order to determine the *enviro-economic cost* of waste processing (EEC). The effect of varying waste composition on the EEC will also be explored. Finally, this work also takes a UK-centric approach where possible, using the country's typical waste composition, utility pricing, and background inventory data for its current waste management scenarios.

4.2 Methodology

4.2.1 Route Description and Modelling

All three gasification routes were modelled using Aspen HYSYS V12.1 with a fixed 550 kt/y feed of MSW, which corresponds to a large-scale gasification plant (Cross et al., 2021a). Four different thermodynamic models were used to determine the stream properties: i) Peng-Robinson in the gasification section and cryogenic distillation train in the methanol-to-olefins section; ii) the Acid Gas-Physical Solvent package for the Rectisol process; iii) NRTL-RK in the low pressure (<10 bar) chemical synthesis sections; and iv) RKSMHV2 in the high pressure (>10 bar) chemical synthesis sections. An overview of the methodology used is presented in Figure 4.2, and an overview of the coupled MSW processes is displayed in Figure 4.3. More detailed diagrams and stream tables of all routes can be found in Section B of the appendices.

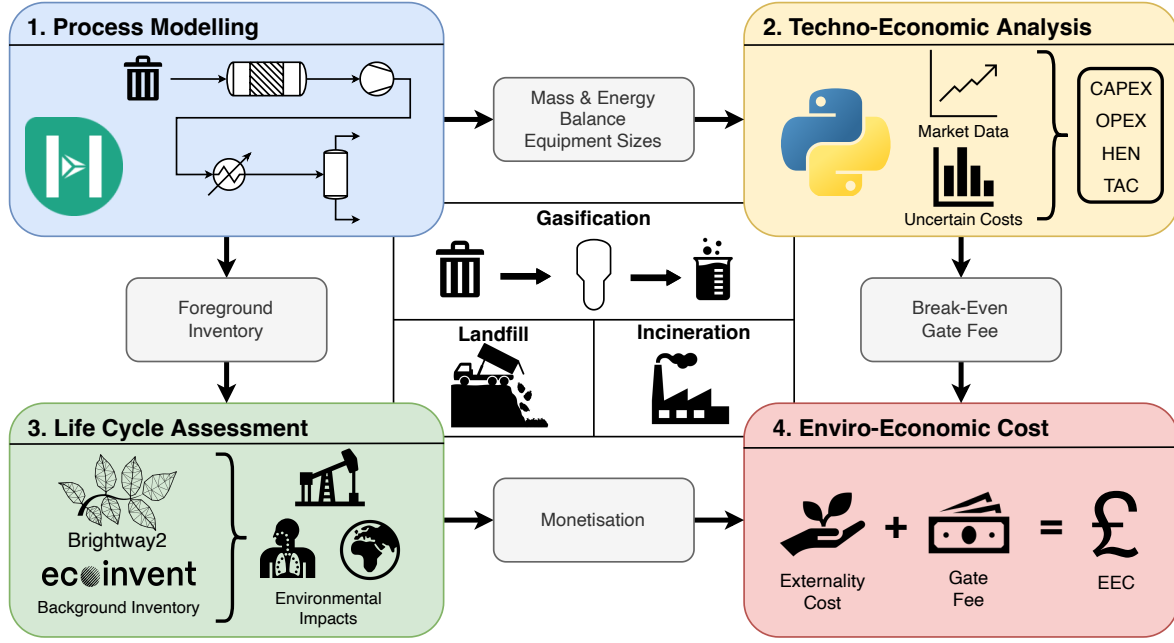


Figure 4.2: Overview of proposed methodology.

Refuse Derived Fuel Preparation

The MSW feed is first sent to a refused derived fuel (RDF) facility for pre-processing. The purpose of this facility is to increase the homogeneity of the feedstock via three main mechanisms: classification, i.e. separating non-combustible materials (e.g., metal, glass, etc); size reduction through grinding; and finally drying (Rotter, 2010). The MSW enters the facility with an average moisture content of 35 wt%, which is typical of MSW in the UK (Cross et al., 2021a). For the classification step, 20 wt% of the MSW feed is assumed to be non-combustible material, and is separated from the waste feedstock (Jones et al., 2009). For the drying stage, it is assumed that the duty from cooling the syngas exiting the gasifier is used to dry the waste to 12 wt% moisture level. The size reduction process via grinding and crushing is not included in the model, but is assumed to require 33 kWh/t of MSW fed into the RDF facility (Nuss et al., 2013). The remaining material is the RDF feed, which is modelled as a hypothetical solid with a fixed elemental composition derived from typical UK waste; importantly, 60% of the carbon in the MSW—and thus in the RDF—is biogenic (Bridgwater et al., 2019b). Refer to Section B of the appendices for the detailed composition of the MSW used in the assessment.

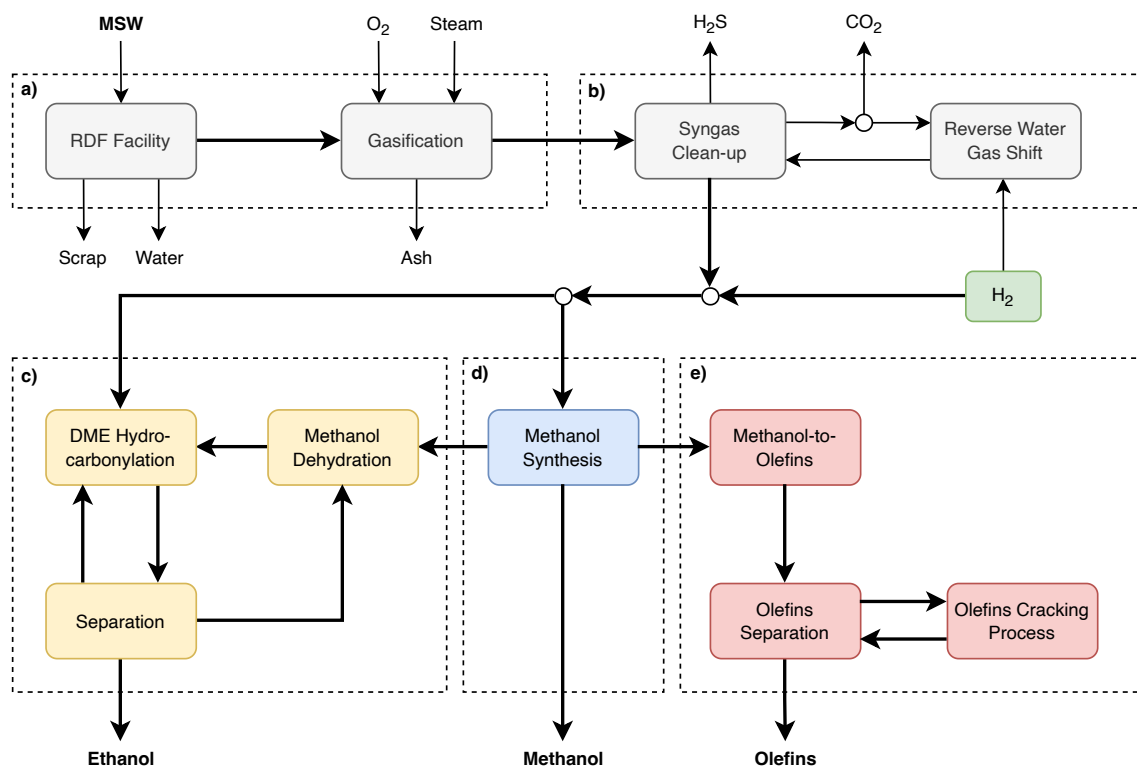


Figure 4.3: Block flow diagram of the three MSW gasification routes with the following sections: a) MSW processing and gasification; b) syngas clean-up; c) ethanol synthesis via DME hydrocarbonylation; d) methanol synthesis; e) methanol-to-olefins.

Gasification

The RDF is fed to a fluidised bed gasifier operating at 750 °C under atmospheric pressure (Griggs and Taylor, 2023). Due to the vast number of reactions and high complexity in gasification processes, it is difficult to model them using kinetic schemes. The gasifier was modelled by combining a conversion reactor and Gibbs' equilibrium reactor into one unit. The conversion reactor first splits the RDF hypothetical solid into its elemental components (carbon, hydrogen, oxygen, etc), using the lower heating value to estimate the required duty. The elemental components are then fed to the Gibbs' equilibrium reactor, where the gasifier products are formed (Puig-Arnau et al., 2010). Since the gasification reaction is autothermal, the energy from the conversion reactor was used as the energy input for the Gibbs' reactor (Pirola et al., 2017).

A mixture of oxygen and steam is used as the gasifying agent as it leads to higher

H₂:CO ratios compared to oxygen or air gasification alone, which is preferable for downstream chemical production (Jordan et al., 2021). The ratio of oxygen and steam fed to the gasifier was adjusted in order to obtain a high CO:CO₂ ratio (2.5:1) in the produced syngas, as well as maintaining the operating temperature in the gasifier at 750 °C. It was assumed that 2% of the carbon in the gasifier remains unreacted to account for carbon losses in the ash (Sun and Tang, 2023) and that all of the sulphur present in the RDF is converted to H₂S (Niu et al., 2013). The produced syngas exiting the gasifier is composed of CO, CO₂, H₂, CH₄, N₂, NH₃ and H₂S, along with ash, which is modelled as another hypothetical component. Although the separation of ash and the formation and subsequent conversion of tars was not explicitly modelled, the cost of the required cyclones for separation and a tar reforming process could still be accounted for in the equipment cost of a gasifier, as described later in Section 4.2.2 (Niziolek et al., 2015a).

Syngas Clean-up

After the produced syngas is cooled (providing the drying duty in the RDF section), it is compressed to 26 bar in a three-stage compression train with interstage cooling and water removal. Before being compressed further and sent to the chemical manufacturing processes, the contaminants in the syngas (mainly H₂S) must be removed to prevent catalyst poisoning. The Rectisol process, which utilises refrigerated methanol as a solvent, was selected as the syngas purification technology, since it can remove H₂S down to less than 0.1 ppmv. It is also the most commonly used syngas purification technology when the downstream process has very high purity requirements (Korens, 2002; Mondal et al., 2011).

The Rectisol process can also remove and recover CO₂ (Yang et al., 2016a), and therefore allows two different syngas clean-up configurations to be investigated: one with and one without CO₂ recycling. In the case with recycling (CCU case), H₂ is reacted with the recovered CO₂ in a reverse-water-gas-shift reactor (RWGS), where the CO₂ is converted to additional CO. The RWGS products can then be recycled and introduced into the compression train. The case without recycling (CCS case) utilises carbon capture

and storage by compressing the recovered CO₂ to 110 bar for pipeline transportation to geological storage (Terlouw et al., 2021a; Salah et al., 2023a). Optimising the CO₂ transport and storage supply chain (Becattini et al., 2022) could also constitute an interesting future research direction.

The clean syngas leaving the Rectisol process is predominately CO and H₂, with small amounts of CH₄ and CO₂, and can be used for chemical synthesis.

Methanol Synthesis

The methanol synthesis section is based on the work by (Van-Dal and Bouallou, 2013). First, the clean syngas is compressed to 78 bar and mixed with additional green H₂ from offshore-wind based electrolysis to obtain an appropriate H₂:CO ratio. A stoichiometric number (S_n) of 2 was used in this work, where SN is defined as follows:

$$SN = \frac{x_{H_2} - x_{CO_2}}{x_{CO} + x_{CO_2}} \quad (4.1)$$

This stream is then heated to 250 °C and fed to an isothermal packed bed reactor filled with Cu/ZnO/Al₂O₃ catalyst, where methanol synthesis (4.2a) takes place alongside the reverse water gas shift reaction (4.2b):



After the reactor, unreacted syngas is separated in a flash vessel and 1% of it is purged to prevent the build-up of inert species, such as CH₄. The rest is recompressed to 78 bar and recycled back to the inlet of the reactor.

The liquid product from the flash vessel is mainly composed of methanol with a small amount of water and unreacted syngas. This stream is subsequently flashed at 10 bar then 1.5 bar to remove most of the unreacted syngas before finally being sent to a distillation column to obtain high purity methanol. The gaseous waste streams (i.e., the purge and distillation column top product) are combusted with oxygen to provide the

heating requirements for the process.

Methanol-to-Olefins

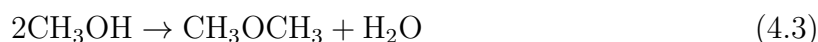
The methanol-to-olefins (MTO) section is based on the UOP/Norsk Hydro process, a high TRL process with a circulating fluidised bed reactor with SAPO-34 catalyst and catalyst regenerator (Chen et al., 2004). In this reactor, the methanol from the previous section is dehydrated at 410 °C and 1.5 bar to form mainly ethylene and propylene, along with higher olefins, alkanes, coke and light gases including CO, CO₂, CH₄ and H₂. This reactor was modelled as a conversion reactor with 100% methanol conversion and with product yields taken from literature (Kuechler and Lattner, 2000; Hannula and Arpiainen, 2015a). The product gas is subsequently cooled and sent to a water quench tower to further cool the gas down to ambient temperature and to remove the bulk of the water.

The quenched product gas stream is then sent to an olefin separation section, which begins with a multi-stage compression train with interstage cooling and water removal with flash vessels. Any remaining traces of CO₂ and water are removed in a caustic wash column and molecular sieve dryer, respectively, to prevent any hydrates forming in the downstream columns. Afterwards, the ethylene and propylene products are recovered and purified via cryogenic distillation, using a front-end deethaniser configuration (Zimmermann and Walzl, 2009). Additionally, the C₄₊ olefins obtained from the bottom of the depropaniser column are sent to an olefin cracking process (OCP), where these higher olefins are cracked to additional ethylene and propylene at 500 °C and 3 bar (Chen et al., 2005). This reactor was modelled using a Gibbs reactor, as the process tends to reach a thermodynamic equilibrium (Vora and Pujado, 2010). The OCP products can then be recycled back to the compression train at the start of the separation section. As in the methanol route, all gaseous side streams streams (e.g. ethane, propane, OCP purge) are combusted to reduce the plant's total heating demand.

Ethanol via DME Hydrocarbonylation

Indirect ethanol synthesis via dimethyl ether (DME) hydrocarbonylation is a route with multiple reaction steps that has a high yield and selectivity towards ethanol. It is increasingly being used in China for coal-to-ethanol processes (Xu et al., 2017) and has also been used in a demonstration plant for waste-to-ethanol by Enerkem (Lynch et al., 2013).

The synthesis starts with the same Rectisol syngas clean-up process as the methanol and MTO routes. However, only 50% of the syngas is sent towards the methanol synthesis section, while sending the rest further downstream towards the hydrocarbonylation section. The produced methanol is then dehydrated on a γ -alumina catalyst to form DME (Bildea et al., 2017):



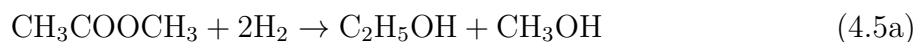
This was modelled using an adiabatic equilibrium reactor with a 275 °C inlet temperature under an operating pressure of 12 bar. DME is separated using a distillation column whilst the water is separated in a second distillation column, allowing unreacted methanol to be recycled. The DME is then sent to the hydrocarbonylation section, where it is mixed with the other 50% of the syngas at 40 bar. This section consists of two packed-bed reactors in series, inside the first of which the DME undergoes carbonylation with CO to form methyl acetate (MA) on an H-MOR catalyst (Cheung et al., 2007):



The carbonylation kinetics were taken from (Diemer and Luyben, 2010). Although these kinetics omit side reactions which can form unwanted CO_2 and CH_4 , a low reaction temperature of 175 °C was used to approximate the conditions where their formation is negligible (Yang et al., 2011; Li et al., 2010). It is also acceptable to pass H_2 through this carbonylation reactor as its only effect on the H-MOR catalyst and carbonylation reaction kinetics is the reduction of CO partial pressure, and thus a slight reduction in

reaction rate (Gao et al., 2018; Yang et al., 2011).

In the second reactor, MA reacts with H_2 to form ethanol and methanol on a copper-based catalyst along with side reactions that form ethyl acetate (Claus et al., 1991):



The hydrogenation kinetics were taken from (Gao et al., 2019) and an adiabatic configuration was used for this reactor, with an outlet temperature set to 250 °C to improve per-pass conversion, whilst minimising the ethyl acetate formation rate. After the carbonylation reactor, additional H_2 is injected to achieve the desired H_2 :MA ratio for the hydrogenation reaction, with a 5:1 ratio selected due to the reaction rate's dependence on H_2 partial pressure. The DME carbonylation reactor was sized for a 70% per-pass conversion of DME, while the MA hydrogenation reactor was designed to achieve 99.9% MA conversion. Typically for the carbonylation reaction, large recycle rates are favoured to increase the reaction rate, by maximising the excess CO and thus partial pressure, which the rate is strongly dependant on (Cheung et al., 2007). In this work, the trade-off between larger reactors and higher recycle flow rates was resolved in favour of the former, although this balance, as well as the relative sizing of the two reaction beds, could be refined through a formal optimisation procedure in future work.

After both reactors, the product stream contains unreacted DME and syngas, as well as ethanol, methanol and some methyl and ethyl acetates. The reaction mixture is cooled down to 35 °C and separated in a flash vessel. The gaseous products are recycled back to the start of the reaction section, after purging a small percentage of the stream to prevent the build-up of inerts (i.e. CO_2 and CH_4 originating from the syngas feed). The liquid product is then sent to a lights stabiliser column, where any remaining DME or syngas remaining is separated and also recycled to the feed of the hydrocarbonylation section.

The liquid product exiting the stabiliser column contains mainly ethanol, methanol and small amounts of the acetates. Most of the ethanol can be separated from the mixture in a distillation column to obtain the final product

The top of this final distillation column contains methanol, the acetates and trace amounts of unrecovered ethanol. This is an azeotropic mixture, with methanol forming azeotropes with both acetates, so an extractive distillation section was used to separate the acetates from the methanol. Without this separation, methanol could not be recycled to the dehydration section to form additional DME as acetates would accumulate. The use of glycerol as an extractive agent allows the complete separation of methanol from the methyl and ethyl acetates (Liu et al., 2023). The methanol can then be recycled to the dehydration section, and the acetates can be mixed with the DME stream leaving the dehydration section to be sent towards the hydrocarbonylation section, where they will both react to form additional ethanol and methanol.

4.2.2 Route Assessment

Techno-Economic Analysis

HysysPy was used to connect to the Aspen HYSYS flowsheets and size the equipment for obtaining the purchased equipment costs. Custom units were defined for the gasifier and RDF facility, where the cost correlations were taken from (Niziolek et al., 2015a), which also includes the costs of cyclones and tar conversion, as discussed in Section 4.2.1. Further information on the correlations used can be found in Section B in the appendices. The capital costs were then annualised using a 20-year lifetime and 10% interest rate to obtain the annualised capital charge (ACC). Since this estimation method of capital costs is uncertain, a triangular distribution on the total capital cost with bounds at $\pm 50\%$ of the nominal value was assumed.

For the operating costs, it was assumed that the site is supplied with uninterrupted renewable electricity from an offshore wind farm, which provided the base electricity demands for the plant (compressors, pumps, etc), as well as green H_2 from electrolyzers. This renewable electricity supply was also used for the heating and cooling utilities, in-

cluding the compression requirements for refrigeration cycles and the heating (assuming both steam generation and high temperature heating are electrified). The cost of electricity was taken as the range from estimated 2025 production costs in the UK for an offshore wind farm (BEIS, 2023a). Since the site requires an uninterrupted supply, a 30% surplus was added to the electricity cost to account for the required long- and short- term storage (Nyhus et al., 2024a). With this surplus, the electricity costs considered in this work range between £59–72 per MWh. The fixed costs of production (FCP) (including labour, maintenance, taxes, etc) were again determined based on the methodology in (Towler and Sinnott, 2022a).

For H₂ production, PEM electrolyzers were used with an efficiency value, and capital and fixed operating costs taken from a central 2025 H₂ pricing scenario in the UK (BEIS, 2021a). The PEM electrolyzers also supply the oxygen required for the both the gasifier and the combustion of the side streams. The H₂ cost was then calculated as a linear combination of these fixed costs and the cost of electricity for operation. The H₂ feedstock cost, along with utility and waste treatment make up the variable costs of production (VCP). The chemical products manufactured by the gasification plants were assumed to be sold at market price to obtain the plant’s revenue (REV). Market price data for olefins, methanol and ethanol were taken over a six-year period from 2018–2023 in order to account for the effect of market variability. All prices were converted to British pounds (£) on a 2023 basis, using the Chemical Engineering Plant Cost Index (CEPCI) for the capital cost calculations and the US and EU Producer Price Indices (PPI) for the chemical markets prices. Further details on the prices used can be found in Section B of the appendices.

All three types of cost can be combined to obtain the total annualised cost of the plant (TAC, £/y):

$$\text{TAC} = \text{ACC} + \text{VCP} + \text{FCP} \quad (4.6)$$

The overall economic metric used in this work for assessing the gasification routes was the break-even gate fee (BEGF, £/kg_{MSW}). This is the gate fee that the gasification plant would have to charge in order to break-even over the lifetime of the plant, accounting for

the sales of chemical products at market value. This is analogous to the levelised cost of production, but from the feedstock's reference point:

$$\text{BEGF} = \frac{\text{TAC} - \text{REV}}{F_{\text{MSW}}} \quad (4.7)$$

where F_{MSW} (kg/y) is the annual MSW feed flowrate.

Uncertainty in the BEGF was evaluated using a probabilistic scenario approach. First, weekly market prices for the chemical products from 2018–2023 defined 313 equally probable market scenarios. Then, triangular distributions were created for the total capital cost and renewable electricity cost (and therefore, the green H_2 cost), which were discretized into 10 bins each. All possible combinations of market, capital, and electricity scenarios (i.e., 31 300 total scenarios) were assigned overall probabilities by multiplying the individual probabilities. Computing the BEGF for each gasification route in each of these combined scenarios then allowed the full uncertainty space to be captured via a Cartesian product of possible cost and market scenarios.

Life-Cycle Assessment

To assess the environmental performance of the routes, a life-cycle assessment (LCA) was performed in accordance to the ISO 14040/14044 standards (ISO, 2006).

Goal and Scope The aim of the LCA is to determine the environmental impacts of processing MSW via gasification coupled with the manufacture of three different chemicals: methanol, olefins, and ethanol. The functional unit was chosen to be “1 kg of MSW processed by the waste management facility”. The system boundaries are therefore a gate-to-gate analysis, starting after the collection and transportation of the waste to the facility and ending with the produced chemical before it is sold to market. A zero-burden approach was applied, where the upstream impacts from the generation and use phase of the waste is ignored. The system expansion methodology was furthermore applied to the chemical products, where each gasification route receives credits for the avoided production of that specific chemical (Finnveden et al., 2009). This also applies to the heat

and electricity generated by the incineration plant. System expansion is the preferred approach in ISO 14044 for handling multi-output systems, as it avoids the need for arbitrary allocation whilst capturing the environmental benefit of displacing conventional production. Given the functional unit of waste management rather than chemical production, crediting the avoided manufacture of displaced products is appropriate for this assessment. Alternative allocation approaches, such as partitioning impacts on a mass or economic basis, would fail to capture the system-level benefits of integrating waste management with chemical manufacturing. Another important consideration in the scope definition is how biogenic carbon was accounted for. As mentioned in Section 4.2.1, 60% of the carbon in the waste stream is biogenic. The assumption in this work is that the biogenic fraction within the produced chemicals counts as sequestered carbon, and as such, a credit was given for the equivalent amount of CO₂ that has been removed from the atmosphere (Nuss et al., 2013; Müller et al., 2020). Another assumption is that these sequestered carbon credits have not already been claimed by an upstream manufacturing process, to avoid double counting. The same methodology was applied to stored carbon in the CCS version of the routes, i.e. a credit is received for the biogenic carbon fraction that has been stored underground. Biogenic carbon accounting commonly employs the -1/+1 approach, wherein CO₂ removal during biomass growth (-1) is balanced against eventual release (+1). In this assessment, sequestration credits are applied to reflect the temporary storage of biogenic carbon within chemical products, consistent with the methodology employed by Nuss et al. (2013) and Müller et al. (2020).

Life-Cycle Inventory HyssyPy was used to construct the life cycle inventory (LCI) data from the Aspen HYSYS flowsheet. This was then connected to background LCI data from the ecoinvent v3.10 database accessed via Brightway2 (Mutel, 2017). Where possible, UK-specific data was used for the background. The full LCI data for the routes is presented in Section B of the appendices.

Life-Cycle Impact Assessment The ReCiPe 2016 method was used for the life-cycle impact assessment (LCIA), which calculates 18 midpoint impacts (including GWP, land

use, water consumption) and aggregates them into three endpoint impacts: damage to human health (HH), damage to ecosystem quality (EQ), and fossil resource depletion (RD) (Huijbregts et al., 2017).

Interpretation To account for uncertainty in the LCA results, a Monte Carlo analysis was performed within Brightway2, where 1000 randomly generated background samples were taken to perform the LCIA. The uncertainty in the background LCI data is determined using a Pedigree matrix, a semi-quantitative representation of a dataset’s reliability, completeness, and temporal and geographical applicability (Weidema and Wesnæs, 1996). Uncertainty in the foreground data could also be taken into consideration as part of future research (Baaqel et al., 2023).

Enviro-Economic Cost of Waste Processing

The endpoint impacts (E_i) obtained from the LCIA were further aggregated using a monetisation methodology proposed by (Weidema, 2015b), where the budget constrained method is used to determine monetary penalties (M_i) for HH, EQ and RD impacts. These factors were also converted to British pounds (£) on a 2023 basis and are presented in Section B of the appendices. Once monetised, the endpoint impacts can then be combined with the BEGF to obtain the *enviro-economic cost* (EEC) of MSW processing:

$$EEC = BEGF + \sum_i E_i M_i \quad (4.8)$$

Business-as-Usual Comparison

The three candidate gasification routes were compared to typical waste management processes to act a business-as-usual (BAU) comparison. The two processes chosen were landfilling with gas recovery for electricity and heat generation (LDF) and incineration with energy recovery (i.e. energy-from-waste, EFW). The gate fees for both routes were taken from a 2023/24 survey on gate fees across the UK, and a triangular probability distribution range was assumed based on the median, minimum and maximum fees reported by (WRAP, 2024a). For the environmental assessment, the appropriate process

flows were extracted from the ecoinvent database. Note that in order to ensure a fair comparison, the same split obtained from the RDF facility in the gasification routes was applied to the incineration base case (i.e. 20% removed as scrap metal, glass, etc).

Another important consideration for the BAU comparison is the effect of taxes, specifically the UK landfill tax for the landfilling route (WRAP, 2024a) and a carbon tax on the incineration route, which the UK government is planning to implement by 2028 (BEIS, 2020a). The landfill tax applied in this work was the 2023/24 tax of £102.1 per tonne (WRAP, 2024a), and the carbon tax was taken at £260 per tonne, which was the 2025 UK government carbon price (BEIS, 2020a). The same carbon tax was also applied to the direct emissions for the gasification routes, but since only 40% of the emissions from both incineration and gasification are fossil-based, only 40% of the CO₂ emissions were taxed.

Waste Composition Variability

The effect of varying MSW composition on the environmental and economic performance of the gasification routes was also investigated. The overall analysis and EEC calculations were repeated with two additional MSW compositions. These compositions were derived using the same MSW data as discussed in Section 4.2.1. One of these compositions (BIO) considers only bio-based wastes (i.e. food, paper, cardboard, garden waste, etc); and the second one (MPW) only considers mixed plastic waste. The BIO and MPW compositions, representing extreme scenarios for MSW composition, can offer a potential range in EEC values for MSW gasification in the UK. Refer to Section B of the appendices for the detailed composition of these additional MSW compositions.

4.3 Results and Discussion

4.3.1 CAPEX

Figure 4.4 shows the breakdown for the estimated installed equipment costs for the three gasification routes in both CCU and CCS variations. Since a factorial method was used to obtain the total capital investment, this figure is also representative of the relative

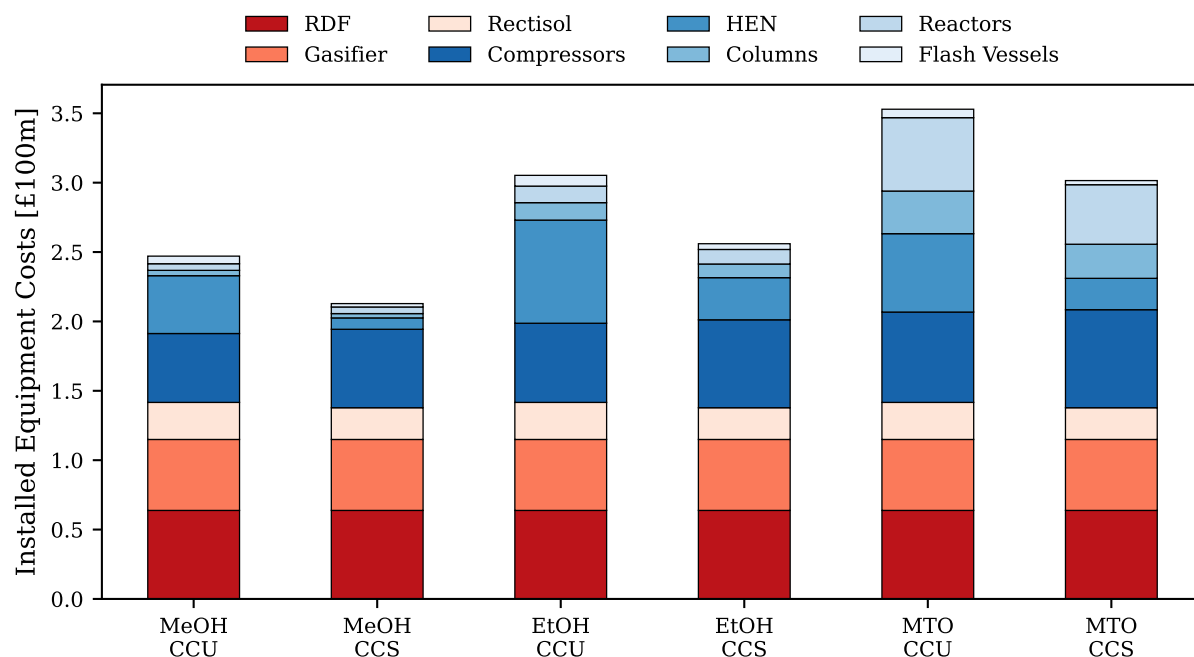


Figure 4.4: Total installed equipment costs for each gasification route in both CCU and CCS variations.

total capital investment between the routes. Even though the absolute values carry up to $\pm 50\%$ uncertainty, the relative assessment is more robust as a consistent methodology has been used across the three routes.

The first trend that can be observed is that the CCS routes have lower capital costs than their CCU counterparts. This is due to a lower syngas flowrate leaving the clean-up section, which leads to significantly lower capital costs in the downstream chemical synthesis sections. The Rectisol section itself is also cheaper in the CCS variants (£23m vs 27m for the CCU variants) without the RWGS reactor and its related recycle stream.

The methanol route has the lowest installed equipment cost in both CCS and CCU variations (£213–247m), followed by ethanol (£256–305m) and MTO (£302–353m). These installed costs correspond to total capital investments of £402–467m, £484–578m and £571–669m, respectively. Across all routes, the cost of the waste processing, gasifier and syngas clean-up sections make up the majority of the overall capital cost (between 40–65% of the total). The RDF facility is the most expensive section in all routes, and is 25% more expensive than the gasifier unit at £64m versus £51m. Other works corroborate this finding, where it was found that the RDF facility made up 25% of the overall

capital costs for a waste to chemicals plant (Jones et al., 2009).

The compressors also form a substantial fraction of the total equipment costs, between £50–70m across the routes. The methanol route only has one compressor train and one recycle compressor, therefore presenting the lowest compressor costs. The ethanol route has additional compressors for the gaseous recycle in the hydrocarbonylation section, and the MTO route has an entire additional compression train in the olefin separation section. Compression costs are also higher in the CCS case due to the additional required CO₂ compression train ahead of transport.

The heat exchanger network (HEN) costs are highest for the ethanol route, at £30–74m versus £8–42m and £23–56m for the methanol and MTO routes, respectively. This is due to the two additional reaction and separation sections for the methanol dehydration and DME hydrocarbonylation, which both have significant heating and cooling requirements. The separation of the alcohol and acetate product mixture in particular has high heating requirements, and there is limited integration potential for the condensers and reboilers of the columns in this section.

The reactor costs are also substantial in the MTO route, which is expected due to the much higher complexity for a circulating fluidised-bed reactor with regenerator compared with packed-bed reactors in the other routes and reaction sections. The column costs are also significantly larger in the MTO route, which is also explained by the high-pressure and cryogenic distillation columns required for the olefins separation section.

4.3.2 Break-Even Gate Fee

Figure 4.5 shows the breakdown of the BEGF for each gasification route and both BAU routes. Note that to obtain this breakdown, the average pricing scenario (i.e. the average electricity price, capital cost estimation and chemical market prices) was used to compute the BEGF. Landfilling has the lowest overall BEGF at £0.13/kg_{MSW}, followed by the three gasification routes with CCS between £0.13–0.16/kg_{MSW}. Incineration is the next most expensive at £0.22/kg_{MSW}, and finally, the three gasification routes with CCU are the most expensive, between £0.26–0.30/kg_{MSW}. These findings are endorsed by Voss et al.

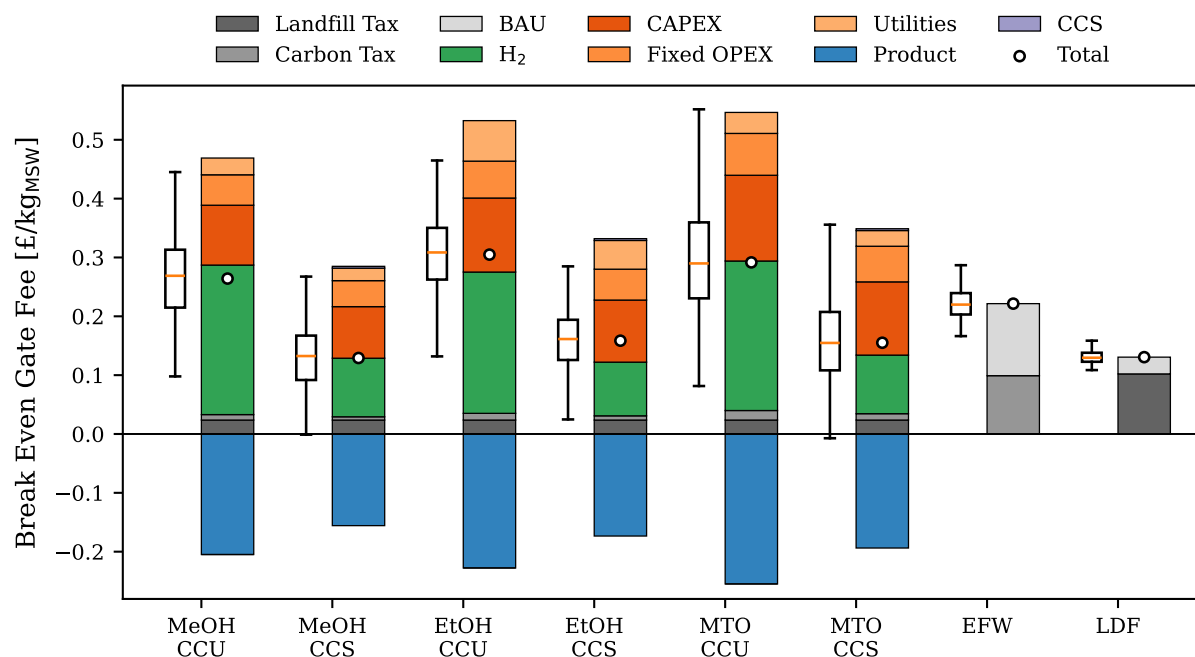


Figure 4.5: Breakdown of break-even gate fee for each route for average price scenario. Bars represent median values; offset box plots show the distribution of break-even gate fees across different economic scenarios (market prices, green electricity costs, and CAPEX estimates), representing scenario uncertainty rather than measurement error.

(2024), who also predicted that landfilling would be the cheapest economically, followed by incineration and finally gasification for methanol production, although they did not consider implementing CCS in the gasification routes.

Similar to the capital cost results, the routes with CCS are significantly cheaper than their CCU counterparts. Removing the CO_2 from the syngas stream reduces the green H_2 demand by 60%, and this reduction more than offsets the cost of CCS (which is almost negligible at the price considered in this work) and the reduced revenues from lower chemical production rates. Even though the CCS routes are cheaper in principle, in reality these results are dependent on the presence of a CO_2 transport pipeline close to the gasification plant. Recovering and recycling the CO_2 as in the CCU case is currently a more feasible option as it does not rely on the establishment of a CO_2 transportation infrastructure.

From the average breakdown of the CCU routes, it is clear that the procurement of green H_2 has the highest contribution in the BEGF, totalling approximately $\text{£}0.25/\text{kg}_{\text{MSW}}$

across all three CCU gasification routes. Reducing the cost of green H_2 by subsequently reducing the cost of renewable electricity or the cost of electrolyzers could therefore lead to a significant reduction in the BEGF for the gasification routes.

Capital and fixed operating costs are other large contributors to the BEGF for the gasification routes, highlighting the capital-intensive nature of MSW gasification plants. The sale of chemicals in the average scenario presented here manages to offset the cost of manufacture and gasification, apart from the H_2 procurement cost. Despite the MTO route having the highest production costs, the olefin products have the highest value, and their sale manages to partially offset these higher costs. The same is observed with the ethanol and methanol routes, which both show a decrease in costs and revenue from chemical sales in both CCS and CCU variations.

For the BAU routes, another important result shown here is the importance that tax has on the overall gate fee. Both the landfill tax and carbon tax contribute c. $\pounds 0.1/\text{kg}_{\text{MSW}}$, which is substantial. Without these taxes, the BAU routes would be significantly cheaper than the gasification routes in CCU variations, and at least competitive in CCS variations ($\pounds 0.03$ and $\pounds 0.12/\text{kg}_{\text{MSW}}$ for landfilling and incineration, respectively). Since only the gaseous waste streams from the gasification routes' chemical synthesis sections are combusted (as opposed to the majority of the MSW feed in the incineration route), the carbon tax contribution to the BEGF is considerably lower, between $\pounds 0.006\text{--}0.016/\text{kg}_{\text{MSW}}$. This highlights the importance of policy interventions for incentivising alternative and more sustainable waste management solutions.

When considering the effect of uncertainty and market variability, the predicted range in BEGF is extremely large for all gasification routes, with the MTO route showing the greatest range from $\pounds 0.08$ to $\pounds 0.55/\text{kg}_{\text{MSW}}$ for the CCU variant and from $-\pounds 0.01$ to $\pounds 0.36/\text{kg}_{\text{MSW}}$ for the CCS variant. However, the interquartile ranges (IQRs) show that the majority of the potential BEGFs exist in a much narrower range. First, in the CCU variation, the MTO route lies between $\pounds 0.23\text{--}0.36/\text{kg}_{\text{MSW}}$; the ethanol route between $\pounds 0.26\text{--}0.35/\text{kg}_{\text{MSW}}$; and the methanol route between $\pounds 0.21\text{--}0.31/\text{kg}_{\text{MSW}}$. In the CCS variation, the IQRs are $\pounds 0.09\text{--}0.17/\text{kg}_{\text{MSW}}$, $\pounds 0.13\text{--}0.19/\text{kg}_{\text{MSW}}$, and $\pounds 0.11\text{--}0.21/\text{kg}_{\text{MSW}}$.

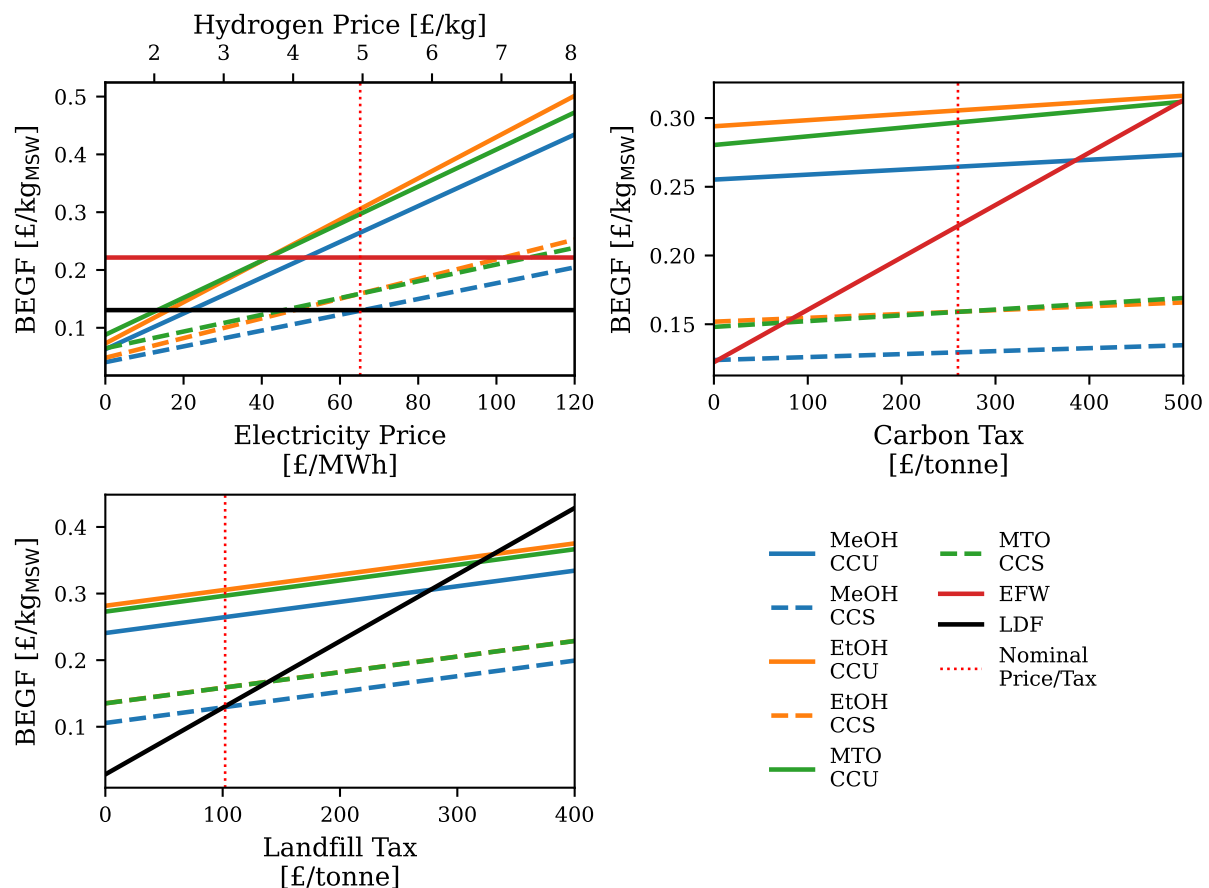


Figure 4.6: Sensitivity analysis of BEGF against renewable electricity and H₂ price (top left), carbon tax (top right), and landfill tax (bottom left).

for methanol, ethanol and MTO, respectively. By comparison, the IQRs for landfilling and incineration are £0.12–0.14/kg_{MSW} and £0.20–0.24/kg_{MSW}, respectively. From comparing the IQRs, it can be concluded that the BEGFs for the three gasification routes with CCU are likely to be up to 50 % greater than incineration, or up to 160% more expensive than landfilling, across market conditions. However, the gasification routes with CCS are much more competitive, with IQRs lower than that of incineration and overlapping with landfilling.

4.3.3 Sensitivity Analysis

Figure 4.6 presents a sensitivity analysis of the BEGF for each route with respect to various economic variables. The top-left plot displays how the BEGF varies with renewable electricity price, which is also a proxy for the green H₂ price. As discussed in Section 4.3.2

earlier, the gasification routes with CCS are already competitive with landfilling at the nominal electricity price of £64/MWh. For the CCU variants to become competitive, the electricity price would have to reduce to £40–50/MWh and £10–20/MWh for incineration and landfilling, respectively. Taking into account the 30% cost increase to account for consistent supply, a recent report from the UK government estimated offshore wind prices could reach £45/MWh by 2040 (BEIS, 2023a). Whilst this does indicate that the CCU variants could be competitive with incineration in the future through electricity cost reductions alone, it is unlikely that they would become competitive with either landfilling or the CCS variants.

The top-right sensitivity plot considers the effect of carbon tax on the routes. Due to the lower direct emissions from all gasification routes, they are less sensitive to a carbon tax than an incineration plant. However, the carbon tax would have to reach between £400–500/tonne before the CCU variants become cheaper, a 50–90% increase compared to the nominal case of £260/tonne. An even larger increase would be required in landfill tax (bottom-left plot) before the CCU variants can compete with landfilling, where an approximately 200% increase from £102/tonne to £300/tonne would be required. Nevertheless, a lower electricity price could also mitigate the necessary carbon and landfill tax hikes, highlighting the importance of advancing technology and policy synergistically for CCU routes to become viable.

4.3.4 Global Warming Potential

Figure 4.7 shows the predicted GWP of the gasification and BAU routes. Recall that for the chosen functional unit (1 kg of MSW by processed by the waste management facility), the zero reference here refers to zero GWP (and other) impacts for processing the waste. The methanol route has the lowest GWP at -1.03 and -0.94 $\text{kg}_{\text{CO}_2\text{e}}/\text{kg}_{\text{MSW}}$ in the CCU and CCS variations, respectively. The MTO route follows with GWPs at -0.84 $\text{kg}_{\text{CO}_2\text{e}}/\text{kg}_{\text{MSW}}$ and -0.80 $\text{kg}_{\text{CO}_2\text{e}}/\text{kg}_{\text{MSW}}$ with CCU and CCS, respectively. The GWP of the ethanol route, between 0.10 – 0.33 $\text{kg}_{\text{CO}_2\text{e}}/\text{kg}_{\text{MSW}}$, is significantly greater. Incineration has a similar GWP to the ethanol route with CCU at 0.32 $\text{kg}_{\text{CO}_2\text{e}}/\text{kg}_{\text{MSW}}$,

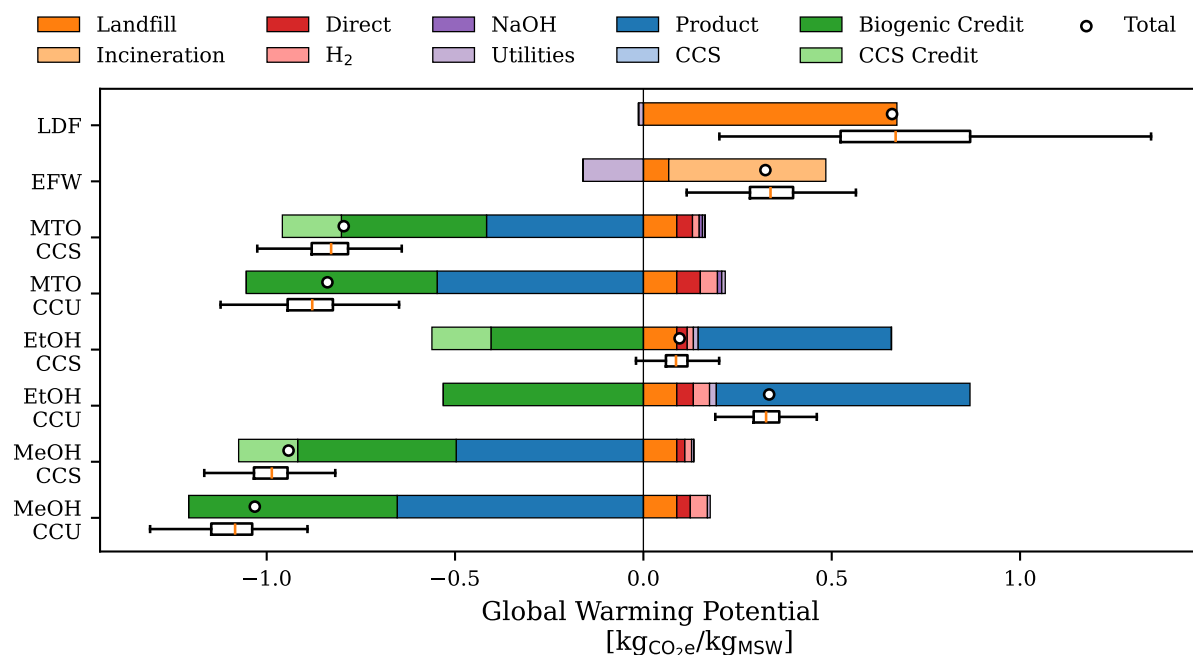


Figure 4.7: Global warming potential breakdown of the gasification and BAU routes. Bars represent median values; offset box plots show the distribution of global warming potential resulting from Monte Carlo sampling of background life cycle inventory data, representing parameter uncertainty rather than measurement error.

and finally the landfilling route has the highest GWP at $0.66 \text{ kgCO}_2\text{e/kgMSW}$.

It is clear that the contributions from the gasification process, feedstocks and utilities are significantly smaller than the avoided impacts of the chemical products. Both methanol and olefins are made from carbon-intensive feedstocks and processes, so there is a significant reduction in GWP when using waste as a feedstock. This finding is verified by the results from Keller et al. (2020), Voss et al. (2024), and Castagnoli et al. (2024), where the substitution of fossil-based manufacturing offered a substantial substitution credit. However, these avoided impacts have the opposite effect on the ethanol route. Since ethanol is typically made via the fermentation of biomass (e.g., wheat, corn, sugarcane), the normal ethanol production route already has a net-negative GWP thanks to the sequestration of carbon within the ethanol product. Avoiding this production route and manufacturing ethanol via MSW gasification instead leads to a net-positive emission of CO_2 , hence the large positive contribution for the ethanol route. Within the context of CO_2 emissions, replacing bio-based manufacturing routes with waste feedstocks loses

its attractiveness.

In contrast, the incineration route benefits from the avoided credits for heat and electricity production, resulting in a lower GWP than the ethanol gasification route. However, as renewable electricity penetration increases in the national grid mix, these credits will reduce, and the GWP of incineration will increase, as Keller et al. (2020) also pointed out. For the landfilling route, methane emissions from the breakdown of organic matter result in a substantial GWP impact, and is the highest out of all the routes even when considering the uncertainty in the background. Even though the landfilling route includes gas recovery and combustion for electricity and heat production, the credits received from this are negligible in comparison to its direct emissions. Refer to Section B in the appendices for detailed assumptions regarding energy recovery from the landfill gas.

The biogenic credits received for sequestering CO₂ are also substantial contributors to the gasification routes, ranging from -0.55 to -0.44 kg_{CO₂e}/kg_{MSW}. Even without this credit through, the methanol and MTO routes would still avoid more emissions from fossil-based manufacturing than is emitted from the processes themselves. However, the GWP of the ethanol route would then exceed that of landfilling.

When comparing the CCS and CCU variations of the methanol and olefins production routes, the CCU ones have slightly lower GWPs. Even though a credit for sequestering biogenic CO₂ is received with CCS, this is lower than the credits received from offsetting a greater quantity of fossil-based chemicals. Again though, this trend is reversed for the ethanol route, where it is beneficial in terms of GWP to offset less bio-based ethanol production, and thus the ethanol route with CCS has a lower GWP than its CCU counterpart.

Taking the analysis further, if only the positive impacts from the gasification routes were considered—that is, neglecting substitution of chemical manufacture and carbon sequestration—their GWPs would still be lower than those of landfilling and incineration. The MTO route would have the highest positive emissions at 0.16 – 0.22 kg_{CO₂e}/kg_{MSW}, due to the higher direct emissions from the combustion of more side streams from the

olefins separation section (i.e. coke, methane, ethane, propane, and the OCP purge). Both the methanol and ethanol routes would have slightly lower direct emissions between 0.13–0.19 kg_{CO_{2e}}/kg_{MSW}. The positive GWP contributions of all gasification routes would also be substantially lower than those of incineration positive contribution (0.48 kg_{CO_{2e}}/kg_{MSW} when omitting substitution of heat and electricity production).

4.3.5 Endpoint Impacts

The results of the endpoint impact assessment for human health (HH), ecosystem quality (EQ) and resource depletion (RD) are displayed in Figure 4.8. All gasification routes have lower HH impacts than the BAU routes, with methanol and MTO with CCS as the lowest two at -6.4×10^{-7} and -5.7×10^{-7} DALY/kg_{MSW}, respectively. They are followed by their CCU counterparts at -5.3×10^{-7} and -4.4×10^{-7} DALY/kg_{MSW}, and then the ethanol routes at 2.8×10^{-7} and 6.7×10^{-7} for CCS and CCU, respectively. Incineration and landfilling come last at 1.5×10^{-6} and 3.2×10^{-6} DALY/kg_{MSW} on average, respectively.

For EQ impacts, all gasification routes are again lower than the BAU routes in terms of species·yr/kg_{MSW}: -3.2×10^{-9} for ethanol with CCU; -3.1×10^{-9} for methanol with CCU; -2.9×10^{-9} for ethanol with CCS; -2.8×10^{-9} for methanol with CCS; -2.7×10^{-9} for MTO with CCU; and, finally, -2.5×10^{-9} for MTO with CCS. The incineration and landfilling routes have the highest EQ impacts at 2.7×10^{-10} and 4.2×10^{-9} species·yr/kg_{MSW}, respectively.

Finally, for RD impacts, both the methanol and MTO routes with CCU have the lowest impacts at $-\text{£}0.214$ and $-\text{£}0.171/\text{kg}_{\text{MSW}}$, respectively. They are followed by their CCS counterparts at $-\text{£}0.164$ and $-\text{£}0.132/\text{kg}_{\text{MSW}}$, respectively. The incineration route has similar RD impacts as the ethanol route with either CCU or CCS, at $-\text{£}0.018$, $-\text{£}0.014$ and $-\text{£}0.013/\text{kg}_{\text{MSW}}$, respectively. Landfilling exhibits the highest RD impacts at $\text{£}0.001/\text{kg}_{\text{MSW}}$.

Both the methanol and MTO routes consistently show the lowest endpoint impacts, owing to the large credits received for displacing fossil-based chemical manufacturing.

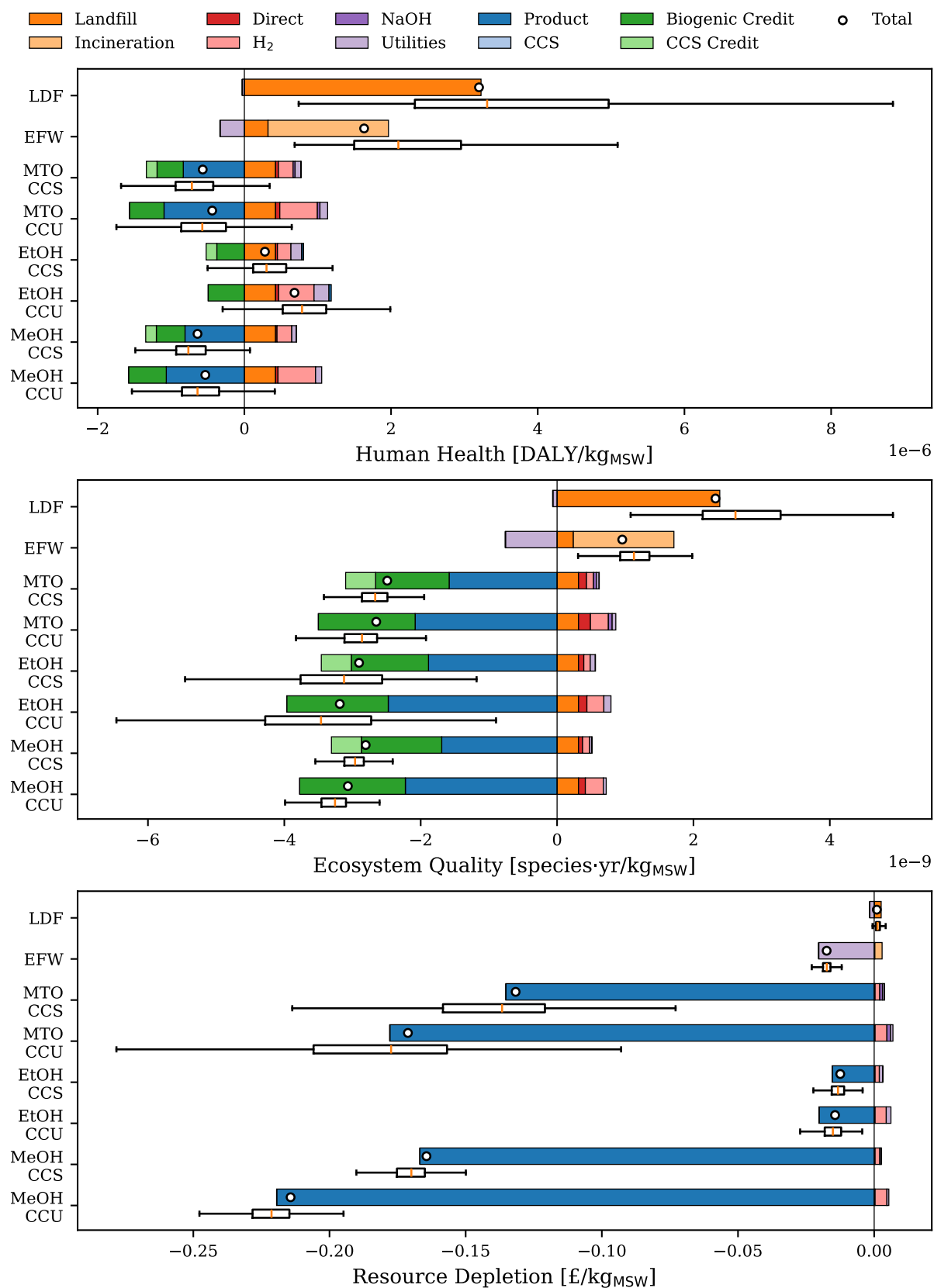


Figure 4.8: Endpoint impacts of the gasification and BAU routes. Bars represent median values; offset box plots show the distribution of endpoint impacts resulting from Monte Carlo sampling of background life cycle inventory data, representing parameter uncertainty rather than measurement error.

For methanol, 67% of the avoided impacts are from the extraction and processing of the natural gas feed for methanol synthesis; the remainder is from the reforming-based synthesis process itself. For the avoided olefins credits, the contribution is swapped: 67% of the avoided impacts are due to steam cracking process—which is one of the most energy intensive processes in the chemical industry (Ren et al., 2006)—whilst the rest is from obtaining the naphtha feedstock. It is evident from these results that large environmental benefits can be obtained from replacing fossil feedstocks with solid waste.

Despite the high midpoint GWP for the ethanol route, the HH impact is relatively lower, and brings the IQR below that of incineration in both the CCS and CCU variations. This is in part due to avoiding fine particulate matter formation from the use of agricultural equipment to grow the biomass source, which helps to offset the high HH contributions due to global warming impacts. The same effect occurs in the EQ impact, where the EQ global warming damage is offset by the large avoided land use impacts from growing the biomass. These results are an example of burden-shifting, and highlight the importance of considering multiple environmental impacts when assessing a process’s sustainability (Finnveden et al., 2009). For the RD impacts, ethanol production again benefits from avoiding agricultural production, this time for avoiding the manufacturing of fertilisers, as well as avoiding the heating demands of the fermentation process. Even though its RD impact is higher than that of incineration, as renewable electricity penetration increases, the credit for avoiding electricity production will reduce in the incineration case, and may result in ethanol having lower RD impacts. The impact of the electricity grid mix should be investigated further in future work, as the results for the incineration BAU route are heavily reliant on a high carbon-intensity grid mix.

As was observed in the midpoint GWP in Figure 4.7, carbon sequestration in the chemical product also offers a considerable credit across all three gasification routes, from -3.7×10^{-7} to -3.4×10^{-7} DALY/kg_{MSW} for HH impacts to -1.1×10^{-9} to -1.0×10^{-9} species·yr/kg_{MSW} for EQ impacts. In the CCS variation, the CCS credit is not as prominent, at -1.5×10^{-7} DALY/kg_{MSW} for HH impacts and -4.4×10^{-10} species·yr/kg_{MSW} for EQ impacts.

Across endpoints and gasification routes, green H_2 shows the largest positive contribution with 5.1×10^{-7} DALY/kg_{MSW} for HH impacts, 2.7×10^{-10} species·yr/kg_{MSW} for EQ impacts, and $£3.4 \times 10^{-3}$ /kg_{MSW} for RD impacts. However, these impacts are from the construction of the wind turbines used to provide the renewable electricity to the electrolyzers, specifically the production of the required iron and steel in the turbine components.

Overall, the difference in HH and EQ impacts between the CCS and CCU variants may not be significant owing to the large overlap between their IQRs. This further illustrates a balanced tradeoff between offsetting more fossil-based chemicals and reducing the impacts from the gasification process itself (especially around green H_2 production). However, there is a substantial reduction in RD impacts when utilising the CO_2 compared to CCS, with a 30% reduction for both the methanol and MTO routes. This reduction is negligible for the ethanol route, as it is only offsetting the fertilisers used in the growth of the biomass.

4.3.6 Enviro-Economic Cost of Waste Processing

Figure 4.9 shows the enviro-economic cost (EEC) of waste processing for each route, which combines both the BEGF and the monetised endpoint impacts that were presented in Figure 4.8. All gasification routes have a lower EEC on average than incineration or landfilling: methanol with CCS is the lowest at $-\text{£}0.21/\text{kg}_{\text{MSW}}$, followed by MTO with CCS ($-\text{£}0.13/\text{kg}_{\text{MSW}}$), methanol with CCU ($-\text{£}0.12/\text{kg}_{\text{MSW}}$), MTO with CCU ($-\text{£}0.02/\text{kg}_{\text{MSW}}$), ethanol with CCS ($\text{£}0.08/\text{kg}_{\text{MSW}}$), and ethanol with CCU ($\text{£}0.27/\text{kg}_{\text{MSW}}$). Incineration and landfilling have the highest EECs at $\text{£}0.46/\text{kg}_{\text{MSW}}$ and $\text{£}0.65/\text{kg}_{\text{MSW}}$, respectively.

For the landfilling BAU route, despite having the lowest BEGF of $\text{£}0.13/\text{kg}_{\text{MSW}}$ on average, it has the highest cost of externalities totalling $\text{£}0.52/\text{kg}_{\text{MSW}}$. The EEC therefore represents a 4-fold increase in cost when environmental damages are considered. For the incineration BAU route, all endpoint impacts are significantly lower than those of landfilling (with credits being received from substituted electricity and heat generation

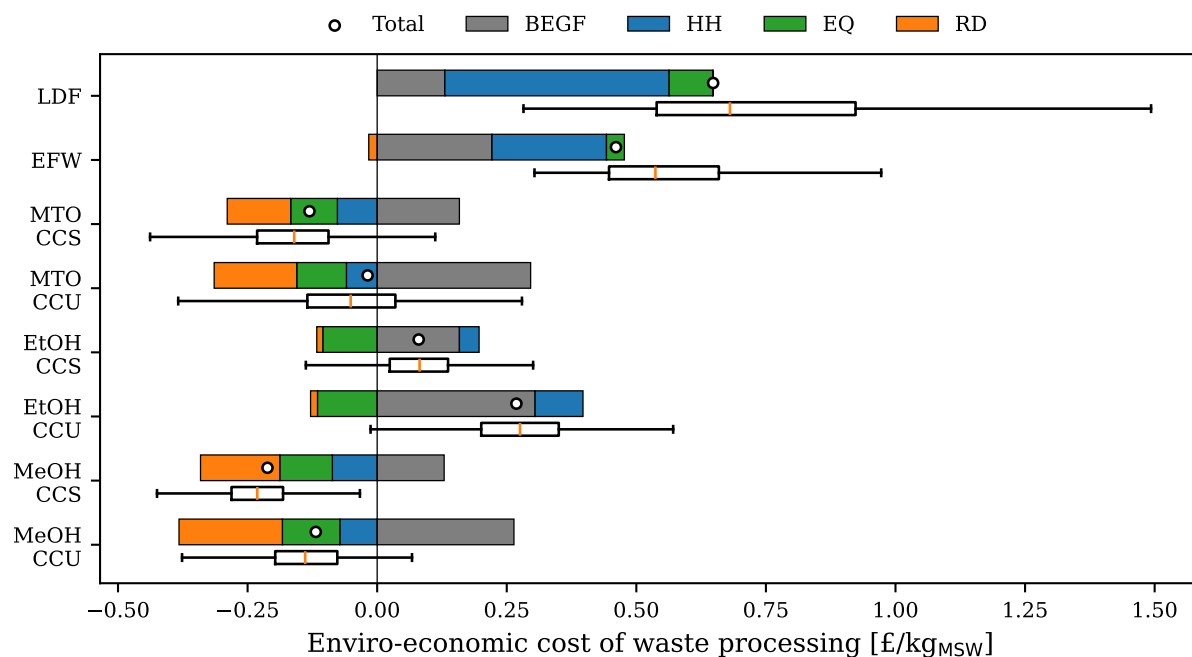


Figure 4.9: Enviro-economic cost of processing 1 kg of MSW for each route, considering both the gate fee and monetised endpoint impacts. Bars represent median values; offset box plots show the distribution resulting from Monte Carlo sampling of background LCI data and varying economic scenarios, representing parameter and scenario uncertainty rather than measurement error.

in RD impacts), resulting in a lower EEC even though the BEGF was almost double by comparison. Here, the EEC is only a 110% increase over the BEGF, but again, as renewable grid penetration increases, the externality costs will likely rise.

The ethanol route has the highest EEC out of the gasification routes, but the EEC is 70% lower in the CCS case than the CCU counterpart. The monetised EQ and RD impacts are similar for both ethanol route variations, but the CCU variant is hampered by a much higher BEGF and HH impacts. This again highlights the care that must be taken when replacing a bio-based chemical with MSW; and in the context of this work, on aggregate it does not appear to be beneficial to maximise ethanol production by utilising the CO₂ in the syngas versus storing it. Nevertheless, both ethanol route variations offer a reduction in EEC over incineration and landfilling.

The MTO route has the second lowest EEC out of the gasification routes considered. Avoiding naphtha cracking for olefins production offers a substantial environmental credit across all endpoint impacts, but the larger credits in the CCU variant are not enough to

offset the higher BEGF, leading to a £0.11/kg_{MSW} lower EEC for the CCS variant. Both present a significant reduction in EEC over the BAU routes, with a £0.48–0.59/kg_{MSW} reduction over incineration, and a £0.67–0.80/kg_{MSW} reduction over landfilling.

Finally, the methanol route has the lowest EECs of all the routes considered. Analogous to the MTO route, the CCS variant has a lower overall EEC compared to the CCU variant due to a significantly lower BEGF. The reductions in EEC relative to the two BAU routes are also significant: £0.79–0.88/kg_{MSW} compared to landfilling, and £0.58–0.67/kg_{MSW} compared to incineration.

When taking into consideration the effect of market conditions and the uncertainty in costs and background LCI data, the EEC IQR for landfilling remains above incineration, between £0.54–0.92/kg_{MSW} compared to £0.45–0.65/kg_{MSW}, respectively. The ethanol route with either CCU or CCS follows with IQRs of £0.20–0.35/kg_{MSW} and £0.03–0.14/kg_{MSW}, respectively. There is more overlap between the remaining methanol and MTO routes, but the general trend in EEC IQRs follows the same ranking as the nominal EEC: MTO with CCU ranges from –£0.15 to £0.04/kg_{MSW}; methanol with CCU lies between –£0.20 and –£0.08/kg_{MSW}; MTO with CCS is the next lowest between –£0.23 and –£0.09/kg_{MSW}; and methanol with CCS is the lowest from –£0.28 to –£0.18/kg_{MSW}. Despite the overlap in IQRs for the methanol and MTO routes, the fact they have the lowest EECs further emphasises the substantial benefit that could be realised by offsetting fossil-based manufacturing with a waste management solution.

The apparent similarity in performance between the methanol and MTO routes in Figure 4.9 reflects the propagation of uncertainties from common modelling assumptions and shared economic drivers. All three gasification routes share common upstream sections (RDF preparation, gasification, and syngas cleanup), meaning assumptions in these shared sections propagate consistently across the routes. Furthermore, all routes are subject to the same dominant economic uncertainty (especially the cost of green H₂) which affects the BEGF similarly.

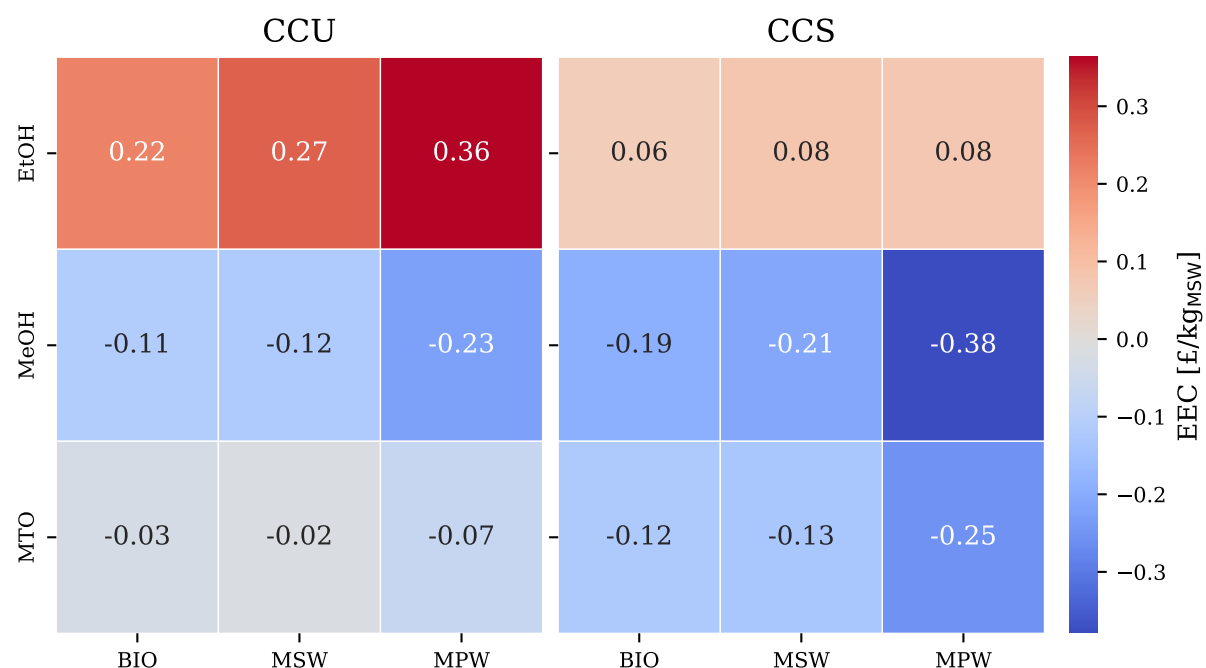


Figure 4.10: Heatmaps of the average enviro-economic cost of waste processing with CCU or CCS for different feedstock compositions.

4.3.7 Effect of Waste Feedstock Composition

Figure 4.10 provides an overview of the effect of different waste compositions on the EEC for the different gasification routes. Comparing the two heatmaps overall, the CCS variants on the right exhibit lower EECs than their CCU counterparts on the left, regardless of the feedstock choice. Again comparing the overall EEC with respect to the chemical product, it also corroborates the findings in the rest of this work that the methanol route has the lowest EECs, followed by the MTO and ethanol routes.

Comparing the ethanol route with the methanol and MTO routes shows opposite trends from the waste composition. It was previously pointed out in Section 4.3.4 that displacing current ethanol production for MSW-derived ethanol would lead to an increase in GWP. Using a fully biogenic waste (BIO) feedstock, therefore, would mitigate the increase in EEC, while a MPW feedstock would worsen the EEC. This is particularly evident in the CCU case, where a fully biogenic feedstock reduces the EEC by £0.05/kg_{MSW} (19%), while using a MPW feedstock raises the EEC by £0.09/kg_{MSW} (33%).

For the MeOH and MTO routes, processing a feedstock with higher biogenic fraction

than the nominal MSW waste would marginally impact the EEC, with only a £0.01–0.02/kg_{MSW} difference. This is since the nominal MSW feed already has 60% biogenic content. In contrast, processing MPW feedstock would significantly decrease the EEC, with the methanol route exhibiting the lowest average EEC at −£0.38/kg_{MSW} in the CCS case. This is due to a more favourable carbon-to-hydrogen ratio in plastics compared to biomass, which results in higher chemical production and lower H₂ supplementation. The higher chemical production increases the credits received from offsetting fossil-based chemicals, while lowering the H₂ supplementation brings the BEGF down. Although using MPW would mean that carbon sequestration credits are no longer received (owing to the absence of any biogenic carbon), the substantial increase in chemical production capacity would more than compensate for the loss of these credits.

4.4 Conclusions

This chapter presented an enviro-economic assessment of chemical production from the gasification of municipal solid waste. The three chemicals considered, i) methanol via CO hydrogenation, ii) ethanol via DME hydrocarbonylation, and iii) olefins via the methanol-to-olefins route, were compared to landfilling and incineration in terms of a break-even gate fee in various market scenarios, as well as in a life-cycle assessment with monetisation of endpoint impacts to obtain an *enviro-economic cost* (EEC) of waste processing. A comparison was also made between removing the CO₂ from the syngas and sending it to storage to reduce H₂ supplementation or recycling it to increase chemical production. Finally, the effect of varying the waste feedstock composition towards either fully biogenic waste or fully mixed plastic waste was assessed in terms of the total EEC.

The results confirmed the capital intensive nature of chemical production coupled with waste gasification. They predicted for all the chemical routes to have greater break-even gate fees than incineration and landfilling when CO₂ is recycled. But sending the CO₂ to storage (CCS) could reduce both the capital expenditure and the amount of additional green H₂ required, to the point that the break-even gate fees would become

cost-competitive. A sensitivity analysis also revealed that a combination of reduced renewable electricity costs and stronger taxation policies (i.e. higher carbon and landfill taxes) would be required to make the gasification routes competitive without CCS.

Environmentally, the gasification routes offer significant benefits compared to incineration and landfilling. The methanol and olefins routes are particularly attractive due to offsetting of their fossil-based counterparts. The benefit is lower for the ethanol route since ethanol is already manufactured from bio-based feedstock. Combining economic and environmental results predicted for methanol production with CCS to have the lowest EEC at $-\text{£}0.21/\text{kg}_{\text{MSW}}$. However, since CCS hinges upon an existing network of pipelines for CO_2 transport and storage, in the short term at least, the non-CCS variants are deemed more feasible. Finally, our findings highlighted how a mixed plastic waste feedstock would significantly reduce the EEC of methanol and olefins, as a lower carbon-to-hydrogen ratio favors higher productivity and lower green H_2 supplementation.

Future work in this area should focus on investigating the effect of gasifier operating parameters (e.g., temperature, equivalence ratio) on the overall EEC of these routes. This is especially relevant for the comparison between CCS and non-CCS variations, where adjusting the $\text{CO}:\text{CO}_2$ ratios in the produced syngas would likely have a large impact on the break-even gate fees. This could be expanded further with optimisation of the gasifier to minimise the EEC depending on the composition of the waste feedstock. Furthermore, the environmental assessment could be expanded by adopting the planetary boundaries framework. Although the monetisation and system expansion approach in this LCA revealed significant potential savings when coupling waste management with chemical manufacturing, it remains to be determined whether these MSW gasification routes would be sustainable in absolute terms. Finally, evaluating the technological, economic, and policy barriers to the adoption of municipal solid waste gasification will be critical to identifying a viable implementation pathway.

Chapter 5

Direct CO₂-to-Ethanol Synthesis

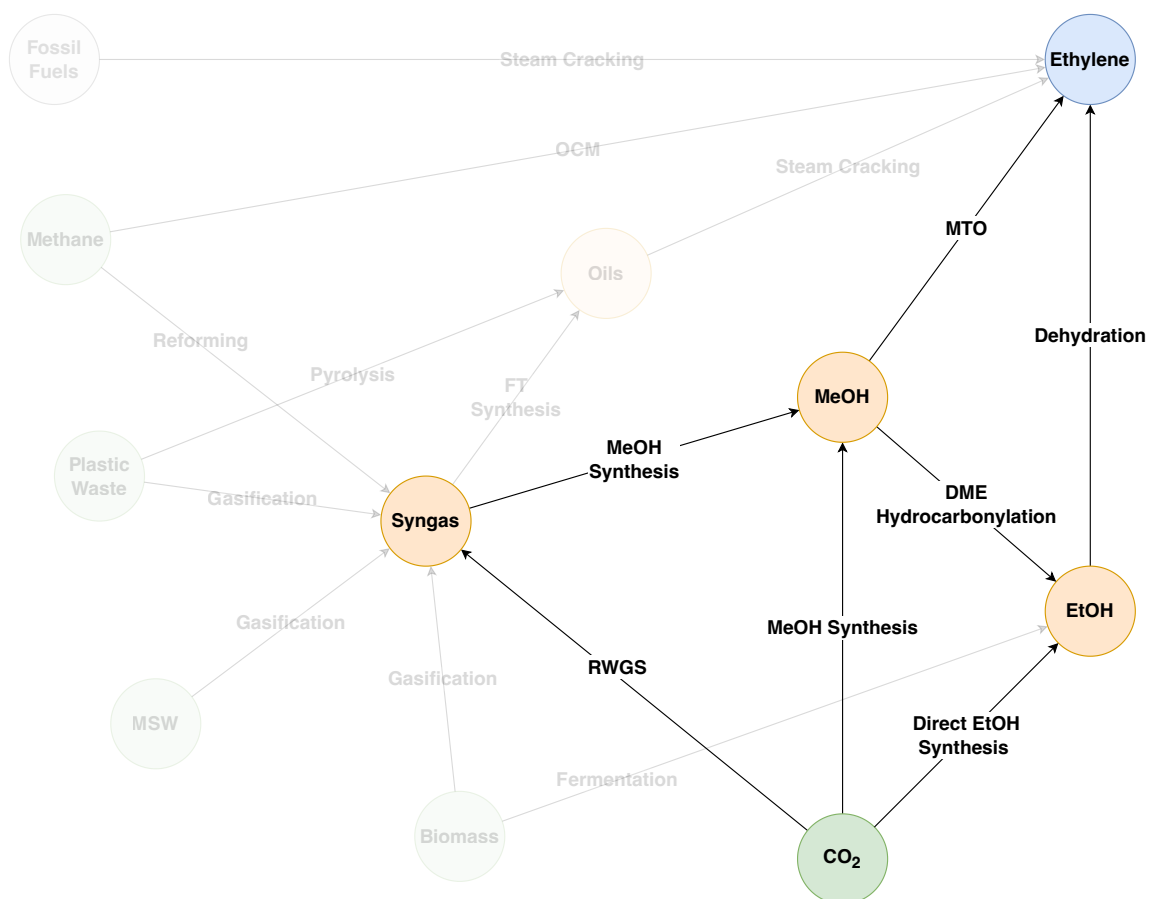


Figure 5.1: Overview of production routes assessed in Chapter 5.

5.1 Introduction

As CO₂ emissions continue to grow in the 21st century, carbon capture and utilisation (CCU) is emerging as one of the potential technological solutions to help keep global warming below 2°C (Al-Mamoori et al., 2017; Gabrielli et al., 2020). Within the context of the chemical industry, not only could CCU reduce emissions from production, but it could also introduce a new carbon feedstock, which would further reduce the reliance on fossil fuels for the manufacture of many valuable chemicals (Baena-Moreno et al., 2019; Bui et al., 2018; Nagireddi et al., 2024). A recent large-scale research project on CCU was the Flue2Chem project, a multi-million pound UK-based project involving 14 different commercial organisations and 2 research institutes (Bott et al., 2025). The aim of the project was to demonstrate the technical feasibility of producing a household good from captured CO₂, the end product of which was chosen to be a surfactant for use in laundry detergents. Specifically, the targeted surfactant is comprised of two main components: the first is dodecanol, a linear alcohol with 12 carbon atoms which acts as the hydrophilic end of the surfactant; and the second are 5-7 ethylene oxide units, which act as the hydrophobic end. Ethylene oxide is manufactured via direct oxidation of ethylene, which itself is typically produced via steam cracking, one of the most energy intensive processes in the entire chemical industry, with over 300 million tonnes of CO₂ emitted globally in 2020 (Amghizar et al., 2020; Ren et al., 2006). For the Flue2Chem project, swapping ethylene production from fossil-fuel based steam cracking to a CCU based process presented itself as an obvious target for demonstrating the feasibility of a CCU-based surfactant value chain.

There already exist routes and pathways to produce ethylene that use CO₂ as a feedstock. The route with the most research and industry focus is the direct hydrogenation of CO₂ to form methanol (Wang et al., 2021). This methanol can then be further dehydrated in the methanol-to-olefins process (MTO), which is already deployed at scale, especially in China where methanol is produced from coal gasification (Tian et al., 2015). In fact, the MTO route is predicted to become one of the foundational pathways in the future decarbonised chemical industry (SYSTEMIQ, 2022).

However, even though methanol synthesis has already been proven at an industrial scale from CO_2 , there is a significant downside of this route when aiming for ethylene oxide production from the context of the Flue2Chem project. The issue is that ethylene is not the only olefin product from the MTO process: propylene and higher C_4+ olefins are produced in parallel, which are not required in the surfactant value chain considered in Flue2Chem. Whilst the ratio of ethylene to propylene produced can be adjusted by controlling the operating severity of the MTO reactor (Chen et al., 2004), or by including an olefin cracking process to convert the higher C_4+ olefins to additional ethylene and propylene (Chen et al., 2005), there is still a significant portion of the product going towards propylene, which is not required for ethylene oxide production. If targeted and on-demand ethylene production is necessary from a CO_2 feedstock, another pathway with higher ethylene selectivity would be desirable.

One method to improve the selectivity towards ethylene is to change the dehydration feedstock from methanol to ethanol. Ethylene is the only major product in ethanol dehydration, which leads to carbon selectivities between 95-99% depending on the catalyst (Morschbacker, 2009). When compared to MTO's typical carbon selectivity towards ethylene of 40% (Hannula and Arpiainen, 2015a; Kuechler and Lattner, 2000), the attractiveness for targeting ethanol from CO_2 becomes apparent. Ethanol dehydration has also been established on an industrial scale, especially in Brazil where cheap ethanol is available from sugar cane production (Jamil et al., 2022).

Whilst ethanol production from alternative feedstocks has garnered a lot of attention in recent years, the majority of research efforts focus on indirect routes for production, typically via syngas (either obtained from gasification, or the reverse-water-gas-shift reaction of CO_2) (Liu et al., 2022; Kanso et al., 2025; Vo et al., 2022) or via methanol, which can be converted to ethanol via dimethyl ether (Zhang et al., 2010; Haro et al., 2012).

Producing ethanol from CO_2 in a single-step, however, is also gaining increased attention, but obtaining it thermocatalytically is significantly more challenging than from methanol. A single-step process could reduce the capital expenditure required by elimi-

nating multiple reaction steps, and thus realise a cheaper production route (Kang et al., 2020). In the literature, there are many efforts being reported on catalyst development for the direct conversion of CO₂ to ethanol (Caparrós et al., 2018; Qian et al., 2015; Boretti, 2024; Zhang et al., 2021; Wang et al., 2018). Whilst ethanol production from CO₂ is thermodynamically more favourable than methanol at industrial operating conditions (Ait El Fakir et al., 2025), the researched catalysts struggle with low ethanol yields and the production of many side products which must be separated (Zhang et al., 2025; Mao et al., 2023). These issues are mainly due to CO₂'s inherent chemical stability and inertness, as well as the difficulty in breaking a C-O bond along with forming a new C-C bond (Pamei et al., 2024).

Whilst progress is being made in the development of these catalysts, there is a lack of studies which investigate their performance if they were deployed at industrial scale. To the best of the authors' knowledge, the only simulation case study that could be found in the literature was work performed by He et al. (2023), where a direct CO₂ hydrogenation to ethanol process was modelled using Aspen Plus. Here, only an ideal set of reactions were considered, which were the conversion of CO₂ and CO to ethanol, and the reverse-water-gas-shift reaction. The effects of reaction temperature, per-pass conversion and purge ratio (i.e. for controlling the fraction of gas recycled to the reactor) were adjusted to determine the potential CO₂ emissions reduction and efficiency of the process. The study did not go beyond these metrics though to investigate the potential economic performance of a direct CO₂ to ethanol process. The lack of any studies on the economic performance of these catalysts raises the question on if such a route would be competitive and viable as a potential CCU technology deployed at scale. It was this question that the Flue2Chem project aimed to answer as one of its objectives alongside the overall feasibility of manufacturing surfactants from CO₂.

As part of the project, BASF had developed a novel catalyst for the direct conversion of CO₂ to ethanol, herein referred to as Catalyst G. The catalyst also produced other alcohols as side products, such as methanol and higher alcohols, but additionally undesired side products such as acetates and methane. The overall aim of this chapter, therefore,

was to take the experimental data for Catalyst G, and then design and model a scaled up CO₂ to ethanol process. The economic performance of the catalyst was then determined, as well as the subsequent economic performance of dehydrating the produced ethanol for ethylene production for use in a CCU-based surfactant value chain. The performance of Catalyst G was also compared to the other current state-of-the-art CO₂-to-Alcohol thermocatalytic processes. Furthermore, theoretical versions of the catalyst with reduced by-product formation rates were assessed to create catalyst development targets with the end-goal of achieving economic competitiveness.

5.2 Methodology

All of the routes were modelled using Aspen HYSYS V12.1, and assumed a 50 kt/y CO₂ feed that was captured using an adsorption process from an industrial point source e.g. a paper mill or cement producer.

5.2.1 Reaction Schemes

High throughput experimentation was performed by BASF to obtain the experimental data at different temperatures, pressures, and CO_x:H₂ ratios. Whilst ethanol was the primary target molecule for Catalyst G, the main products consisted of a range of alcohols, from methanol up to n-butanol. Undesired side-products and intermediates were also formed, including various acetates, and alkanes, especially methane.

In total, 18 reaction data sets were provided by the catalyst development team: 4 considering a pure CO carbon feed, 2 with a mixture of CO and CO₂, and 12 with a pure CO₂ feed. The temperature and pressure conditions considered for these data sets ranged from 270-300°C and 30-80 bar, respectively. Each reaction data set contained the measured inlet and outlet flows for each species, but due to experimental measurement error, the atomic balances for carbon, hydrogen and oxygen for each data set did not balance, and, consequently, neither did the mass. Since the mass must balance when defining reaction schemes in Aspen HYSYS, an optimisation procedure was used to adjust

the molar flows of each reaction species to ensure the carbon, hydrogen, and oxygen atomic balances were conserved. The inlet flowrates of CO, CO₂, and H₂ were taken to be the correct reference values, and adjustments were only made to the outlet flows. The objective function of this problem was to minimise the sum of square differences in flows from the experimental data and the corrected values, whilst subject to the constraint that the atomic balance error for each atomic species must be zero. The optimisation problem was formulated as follows:

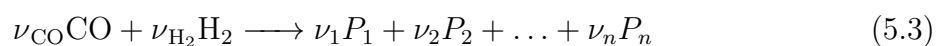
$$\begin{aligned}
 \min_{\alpha_s} \quad & \sum_s (\alpha_s - 1)^2 \\
 \text{s.t.} \quad & \sum_s n_{a,s} (\alpha_s F_{out,s} - F_{in,s}) = 0 \\
 & \forall a \in (C, H, O)
 \end{aligned} \tag{5.1}$$

Where the $n_{a,s}$ is the number of atoms of C, H, or O in species s , and α_s is the adjustment factor for the outlet flowrate of species s . This was implemented using Pyomo (Bynum et al., 2021), and solved using Gurobi v12.01 (Gurobi Optimization, LLC, 2025) for each of the 18 reaction data sets, and the solutions revealed that a maximum adjustment factor of 15% was needed across all species and reaction sets to ensure atomic balance.

Once the corrected outlet flows were obtained, the reaction scheme was developed for each data set. In the absence of full kinetic data, two conversion reactions were defined; the first was the reverse-water-gas-shift (RWGS) reaction, which is assumed to be the only reaction that CO₂ takes part in.



The second is a global CO-to-X hydrogenation reaction, where the CO formed from the RWGS reaction (and any additional CO present in the feed) reacts with H₂ to form all of the product species (i.e. alcohols, acetates, alkanes, water etc).



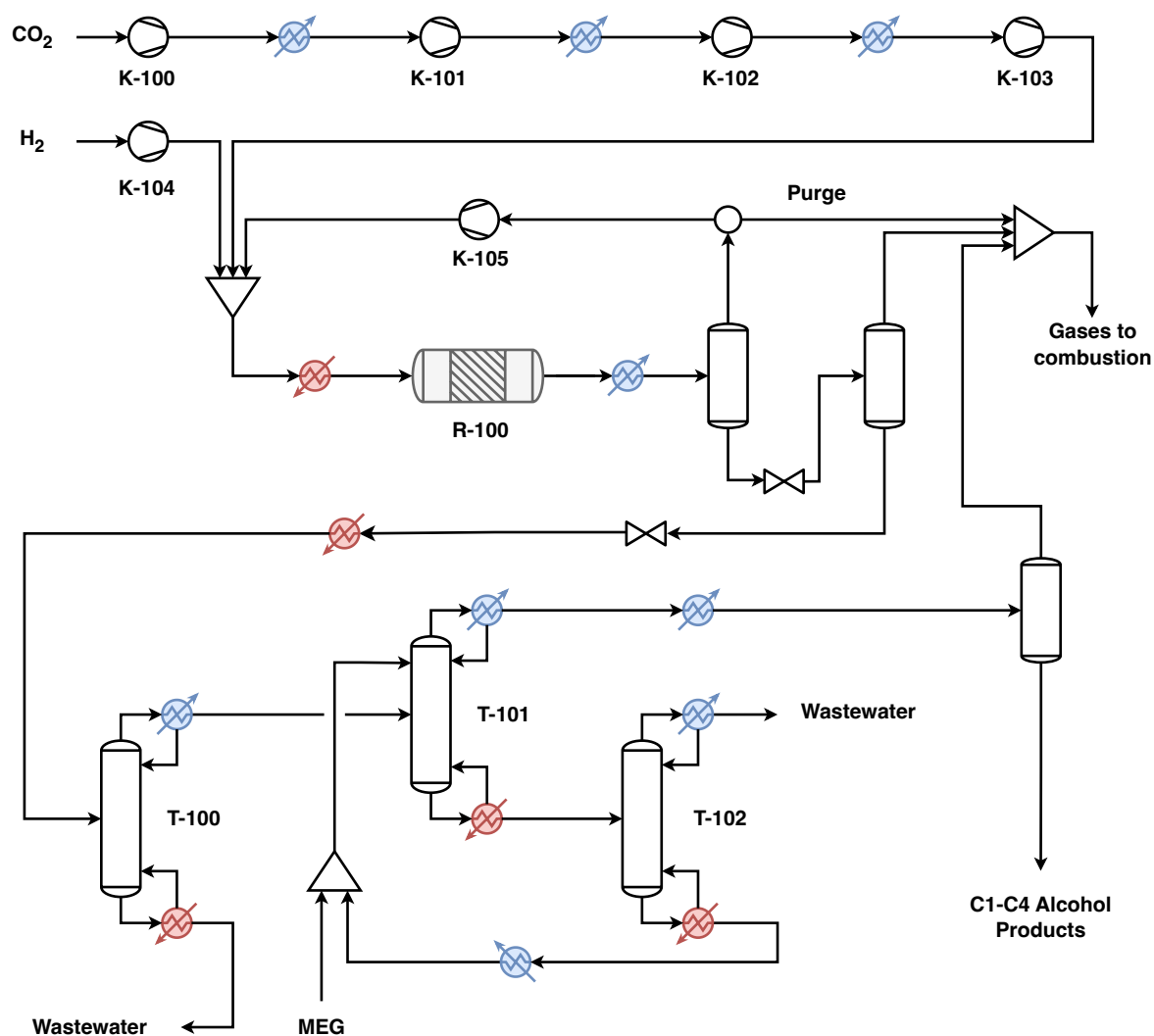


Figure 5.2: Process flow diagram for the Catalyst G Base Case route.

For each data set, the stoichiometry coefficients for reaction 5.3 were calculated from the corrected experimental molar flows, as well as the conversion rates. This overall process therefore resulted in 18 different reaction sets that could be implemented in Aspen HYSYS to represent the scaled-up process.

5.2.2 Catalyst G Route Descriptions

Base Case

The first route considered for Catalyst G is the Base Case (or G-BC) route, for which a process flow diagram is shown in Figure 5.2. This route starts with the captured CO_2

passing through a four-stage compression train with interstage cooling (K-100 to K-103) to reach the desired pressure, depending on the selected reaction scheme (i.e. between 30-80 bar). The green H₂ feed is also compressed up to reaction pressure in a separate compressor (K-104), and its flowrate is adjusted to obtain the desired CO_x:H₂ ratio as specified by the chosen Catalyst G reaction scheme. Since the H₂ is produced via water electrolysis, it is assumed to be available at 30 bar, and therefore needs at most one additional compressor to reach reaction conditions (Colella et al., 2014). The CO₂ and H₂ are then mixed and heated up to the desired reaction temperature (i.e. 270-300°C), before being fed to the Catalyst G reactor.

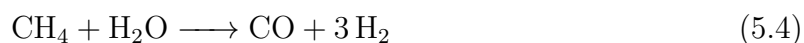
This reactor (R-100) is an isothermal packed bed reactor that is modelled as a conversion reactor with reactions 4.2b and 5.3 specified within it. The reactor is specified with a fixed gas-hourly-space-velocity (GHSV) of 3000 h⁻¹, which is the same GHSV used to obtain the catalyst data. This GHSV value also allows the volume of the reactor to be determined for cost calculations, which are described in Section 5.2.4. The products from the reactor are then cooled to 35°C and the liquid and gaseous products are separated in a flash column. The gaseous stream, which mainly consists of CO_x, H₂ and CH₄, are first sent to a purge splitter, where a certain percentage of the stream is removed and combusted to provide heating for the rest of the process. From the experimental data, the selectivity and yield of CH₄ is relatively high for all reaction schemes, and in many cases is higher than that of alcohol production. To prevent CH₄ from excessively building up in the reactor feed stream, the purge rate was adjusted to prevent the CH₄ composition from exceeding 10mol%, a limit which was set after discussion with internal catalyst experts at BASF. The unpurged gases are then recompressed in compressor K-105, and recycled back to the feed of the packed bed reactor.

The liquid products from the flash vessel consist of water, mixed alcohols, and various unwanted side products (e.g. acetates). The liquid product stream is flashed in another vessel at 10 bar to remove any dissolved gases, and then sent to a dehydration section. Here, the water is removed from the rest of the liquid products in two stages. First, a standard distillation column (T-100) is used to remove >90% of the water, after which

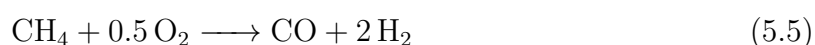
the various azeotropes that are formed between water and the alcohol products prevent further distillation. To break the azeotropes and remove the remaining water down to 1%, a monoethylene glycol (MEG) process is implemented, which consists of two columns: an absorber (T-101), which strips the water from the liquid mixture using the co-fed MEG; and the regenerator (T-102), where the water is removed from the MEG, which can subsequently be recycled (Miranda et al., 2020). A small make-up flow of MEG is required to account for losses in the regenerator water outlet stream. The top liquid product from the absorber passes through one final flash at 35°C to remove any final dissolved gases, leaving behind the predominantly C1-C4 alcohol product mixture. This alcohol mixture is then ready for transportation, separation and further potential processing.

CH₄ Pre-reactors

Due to the high CH₄ formation rates present in the G-BC route, two additional process arrangements were investigated for Catalyst G with the aim of converting the produced CH₄ into additional syngas. This will result in a lower purge rate compared to the G-BC route, at the expense of a more complicated and expensive process. Both of these additional arrangements involve an additional pre-reactor at the start of the process, where CO₂, H₂, and the recycled gases are fed. The two pre-reactors investigated were: a reverse-water-gas-shift reactor (G-RWGS); and a tri-reforming of CH₄ (G-TRM) reactor. In the G-RWGS option, the fed CO₂ is converted to CO in the RWGS reaction. Additionally, the steam CH₄ reforming reaction takes place as a side reaction, which is common in RWGS catalysts, and therefore consumes excess CH₄ in the recycled gases (Wittich et al., 2020).



In the G-TRM option, O₂ is also co-fed to the pre-reactor, which introduces the partial oxidation of CH₄ (Song and Pan, 2004).



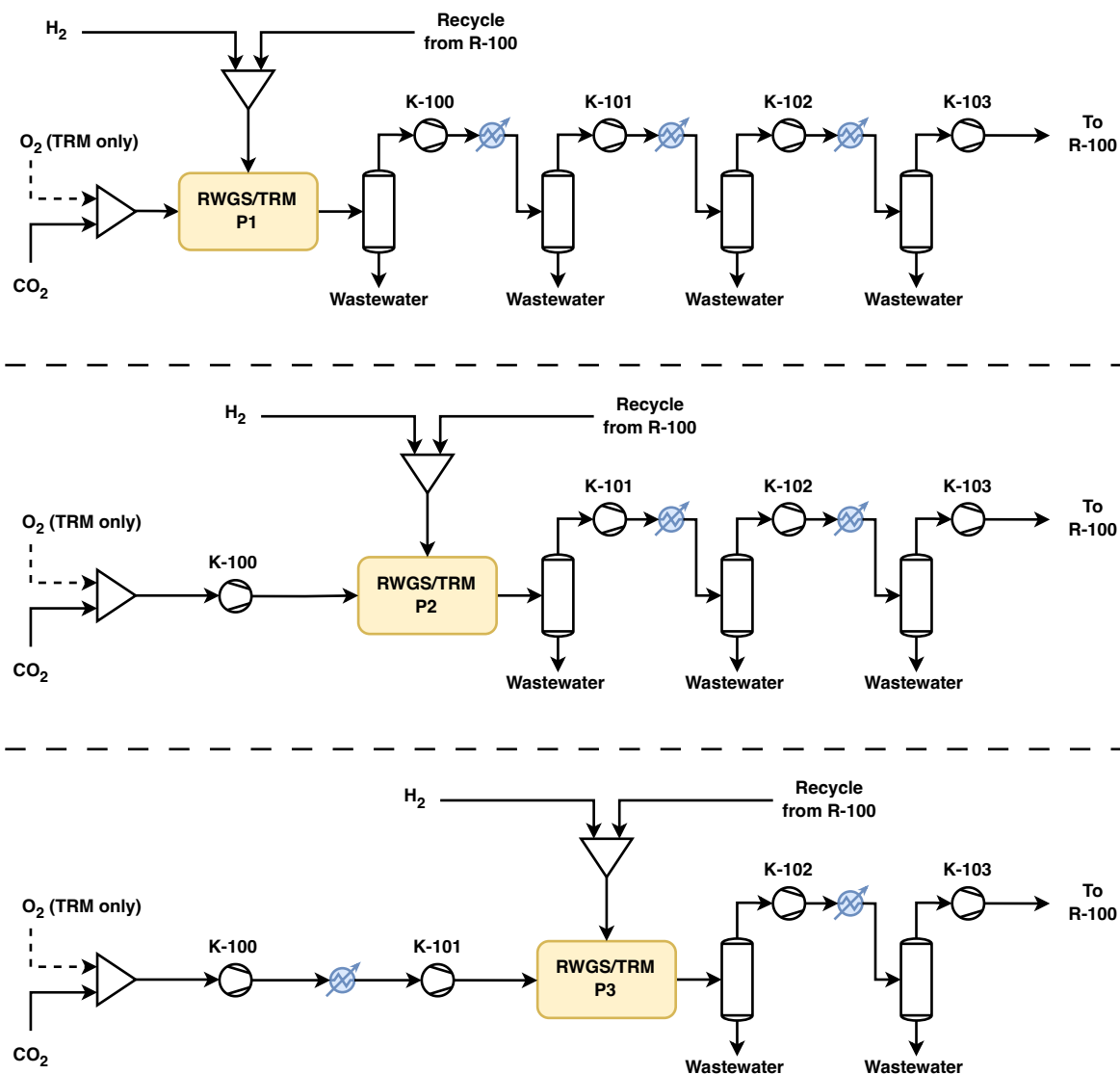


Figure 5.3: Process flow diagram of RWGS and TRM pre-reactor configuration for Catalyst G routes with different potential pressure locations for the RWGS/TRM pre-reactor.

The expected benefit of the TRM reactor over the RWGS reactor is the exothermic partial oxidation of CH₄ will offset the highly endothermic RWGS reaction, and thus reduce the heating demand for the pre-reactor section. The flowrate of O₂ in G-TRM was therefore adjusted until the operation of the TRM reactor was autothermal. However, both still operate at 850°C and thus require substantial pre-heating and cooling (Busca et al., 2024). Both of these pre-reactors were modelled as equilibrium reactors within Aspen HYSYS, with reactions 4.2b and 5.4 defined in G-RWGS, and reaction 5.5 also defined in G-TRM.

On top of the choice of pre-reactor, the pressure level in the compression train where

the pre-reactor is located was also investigated. Changing the operating pressure of the pre-reactor highlights two contrasting effects. The first considers the duty required for compression, where the lower the pressure of the pre-reactor, the larger the compression will be as the gaseous recycle stream from R-100 is fed to a lower pressure level. On the other hand, the lower the pressure, the higher the equilibrium conversion will be for the CH_4 removal reactions due to Le Chatelier's principle (Abbas et al., 2017).

Figure 5.3 summarises the changes required to the feed section of G-BC to incorporate the pre-reactors, as well as the different pressure locations that the RWGS/TRM pre-reactors can be located. In the G-TRM case, the O_2 is mixed with the CO_2 feed at the start of the process, whereas the H_2 and recycled gases from R-100 are fed directly to the pre-reactor in both G-RWGS and G-TRM. Note that additional knockout vessels are also added before each compressor to remove the water generated by the pre-reactors. The rest of the process flow diagram is identical to that of G-BC, except the first water removal distillation column, T-100, is no longer required as the majority of the produced water has already been removed by the knockout vessels in the compression section.

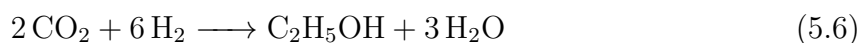
Considering the first three pressure levels as potential locations for the RWGS or TRM pre-reactor, there are 12 total models each for G-RWGS and G-TRM when combined with the 4 CO-based Catalyst G reaction schemes. Note that the fourth pressure level was not considered as a potential location as initial modelling and testing revealed that conversion rates of CH_4 were too low to offer any benefit over the G-BC case.

Comparison

The performance of the Catalyst G routes was compared to other CO_2 to alcohol routes that exist at a higher TRL level. These were also modelled within Aspen HYSYS with the same fixed 50kt/y feed. These routes were direct and indirect CO_2 hydrogenation towards methanol (MeOH-D and MeOH-IN, respectively), and indirect ethanol synthesis via dimethyl-ether hydrocarbonylation (EtOH-DME). The methanol synthesis route acts as the current state-of-the-art option for CO_2 utilisation towards alcohols as it has already been deployed at TRL level 9 (Wang et al., 2021). The indirect version of methanol

synthesis refers to the presence of a RWGS pre-reactor, which, similarly to the G-RWGS and G-TRM options, can be located at various pressure levels in the feed compression train. The work by Van-Dal and Bouallou (2013) was used as the basis for the MeOH-D route, and the MeOH-IN route was created using the same methodology as the G-RWGS route when compared to the G-BC route i.e. a RWGS pre-reactor was added at one of the three pressure levels in the feed compression section. The EtOH-DME route is a multi-stage process that is currently used in China in their coal-to-ethanol process (Xu et al., 2017), and acts as the current state-of-the-art thermochemical process for syngas to ethanol. The route benefits from high selectivity and yield towards ethanol, but requires very high capital investment due to multiple reaction and separation sections, along with very high recycle rates (Liu et al., 2022). The EtOH-DME route model is the same as was described in Chapter 4.

Additionally, a hypothetical CO₂-to-Ethanol route (HYPO) was modelled. This route considered 100% selectivity towards ethanol via direct CO₂ hydrogenation, and equilibrium conversion at the lowest temperature and pressure combination of the investigated conditions from the catalyst experiments i.e. 30 bar and 270°C:



The purpose of this route is to act as a theoretical target for CO₂-to-Ethanol catalytic performance, and therefore presents as an upper bound for Catalyst G in this work.

5.2.3 Olefins Production

The Catalyst G and comparison routes can all be described as CO₂-to-Alcohol (C2A) plants. In this work, the effect of producing olefins from these alcohols was also investigated, by assuming that a certain number, N, of a specific type of C2A plant were used to feed a centralised olefin production facility. By default, this work considered a total of 10 C2A plants that fed this centralised olefins facility, each of which consumes the 50 kt/y feed of captured CO₂. The produced alcohol mixture (or methanol and ethanol for

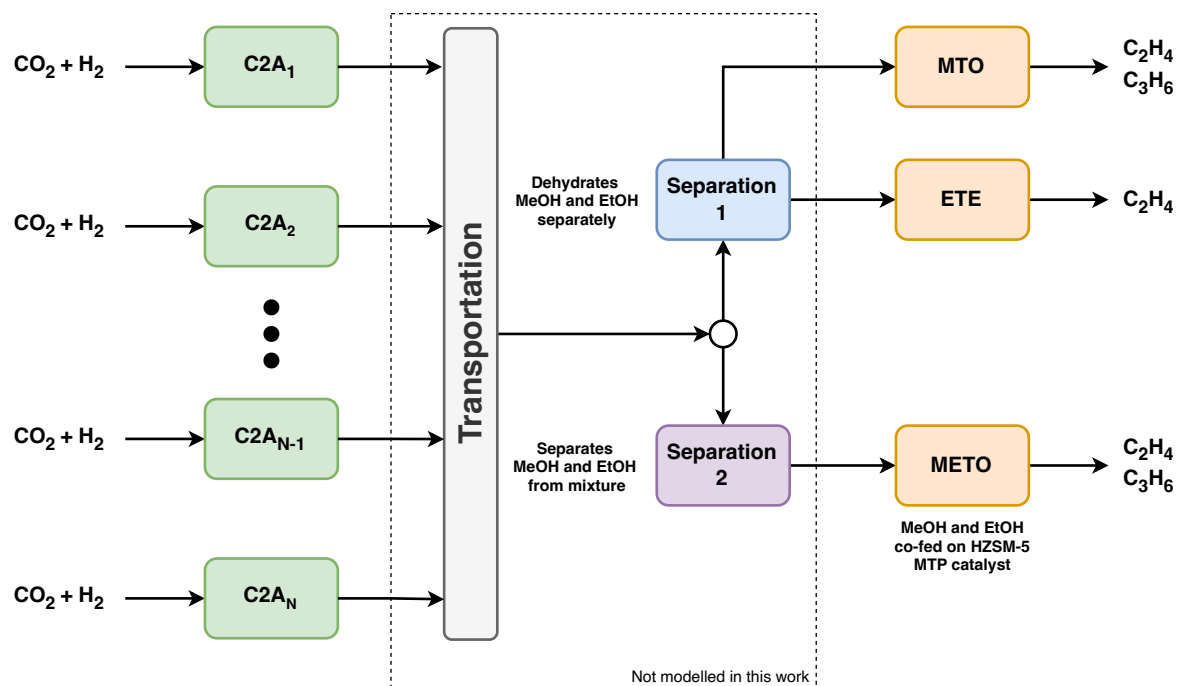


Figure 5.4: Block flow diagram of CO₂-to-Olefins (C2O) value chain.

the comparison routes), is transported to this centralised olefin production facility, which has two configurations: separate dehydration, or co-fed dehydration.

In the separate dehydration option, the main produced alcohols (i.e. methanol and ethanol) are recovered and dehydrated separately. This involves a combination of a methanol-to-olefins (MTO) plant, and an ethanol dehydration plant to form ethylene (ETE). The MTO process route produces both ethylene and propylene as the final olefin products, and includes an olefins cracking process (OCP) to increase the yield of these light olefins (Vora and Pujado, 2010). The MTO model employed here is the same as described in Chapter 4 and the ETE plant is described in Chapter 3.

In the co-fed option, methanol and ethanol are recovered together and are dehydrated simultaneously on a HZSM-5 Methanol-to-Propylene catalyst. Yield information for this reactor was taken from work by Feng et al. (2020), where the reactor product distribution is adjusted depending on the ratio of methanol and ethanol fed. This catalyst also benefits from lower coke formation compared to the SAPO-34 catalyst used in the MTO process, so has a slightly higher carbon efficiency (Schulz, 2010). This co-fed reactor was modelled as a yield-shift reactor in Aspen HYSYS, and similar to the MTO process, includes an

OCP to increase the yield of ethylene and propylene as the desired end products. Further details on this route can be found in Appendix C. The expected benefit of the co-fed option is a reduced capital investment from constructing only one olefins production plant, instead of two in the separate configuration.

A summary of these options and the whole CO₂-to-Olefins (C2O) value chain is shown in Figure 5.4. Note that in this work, the transportation costs for the alcohol mixture to the olefins plant and the separation costs of the alcohols were not considered.

5.2.4 Route Assessment

Efficiency Metrics

Two process efficiency metrics were calculated for preliminary analysis of the C2A routes. The first was the carbon efficiency i.e. the percentage of carbon atoms from the CO₂ feed that was present in the alcohol products, which considers the C1-C4 alcohols:

$$C_{eff} = \frac{\sum_a n_{C,a} F_a}{F_{CO_2}} \quad (5.7)$$

where $n_{C,a}$ is the number of carbon atoms per mole of alcohol a , and F is the molar flowrate of the alcohols or CO₂. Additionally, the energy efficiency of the C2A plants was also determined. This considered the energy within the alcohol products as a percentage of the overall input energy, which includes electrical energy (e.g. from compressors), external heating, and the embedded energy within the green H₂ feed:

$$E_{eff} = \frac{\sum_a LHV_a F_a}{Q_H + W_E + LHV_{H_2} F_{H_2}} \quad (5.8)$$

where LHV is the lower heating value, Q_H is the external heating demand (i.e. total fired heat and steam heating requirements for the C2A plant), and W_E is the total electricity demand.

Techno-Economic Analysis

All costs used in the techno-economic analysis (TEA) were adjusted to USD on a 2023 basis. The total capital investment (TCI) for each C2A and C2O route was determined using HysysPy. For the Catalyst G reactor, the GHSV was used to determine the required volume of a packed bed reactor, which is then costed as a pressure vessel according to the same methodology described in Towler and Sinnott (2022a).

$$V = \frac{Q_{feed}}{GHSV} \quad (5.9)$$

where V is the volume of the reactor in m^3 and Q_{feed} is the volumetric flowrate of the reactor feed in m^3/h . The RWGS and TRM pre-reactors were costed using the correlations from Ordóñez et al. (2022) and Graciano et al. (2018), respectively. The annualised capital charge (ACC) was then obtained from the TCI by assuming a 20 year lifetime of the plant, and a 10% interest rate. Additionally, since the calculation of capital costs at an early stage assessment are uncertain, a $\pm 50\%$ triangular uncertainty distribution was assumed over the nominal calculated ACC.

For the variable costs of production (VCP), European market prices from the period 2018-2023 were used for the chemicals (methanol, ethanol, ethylene and propylene), and UK market prices were used for electricity, and natural gas, which was used for high temperature heating requirements after heat integration (Polymer Update, 2024; Trading Economics, 2025). H_2 was assumed to come from PEM electrolyzers powered by wind electricity, where a low, central, and high production price (5.2, 7.6, and 15.8 \$/ton, respectively) was used to construct a triangular distribution of potential H_2 prices (Parkinson et al., 2019). Note that it was assumed that there was only enough renewable electricity to produce the H_2 and the rest of the plant electricity demand had to be met with grid electricity, hence the inclusion of UK electricity prices. The captured CO_2 cost was taken from an assumed capture cost from a cement plant, with a uniform distribution between \$78/tonne and \$156/tonne (IEA, 2021).

Fixed costs of production (FCP), such as maintenance, labour, and taxes, were also

estimated using the methodology from Towler and Sinnott (2022a). Combining the ACC with both the VCP and the FCP allowed the total annualised cost of production for the plants to be calculated (TAC):

$$TAC = ACC + VCP + FCP \quad (5.10)$$

The TAC was calculated for both the individual C2A plants, as well as an entire C2O value chain i.e. the combined costs of 10 C2A plants that feed their produced alcohol mixture to a single separate or co-fed olefins production facility.

Green Premium

Since various alcohol products are being produced from the different C2A plants, and two different olefins are the final product in the C2O routes, a metric called the “Green Premium” (GP) was derived to easily compare the overall economic performance of each C2A and C2O route. The GP is defined as the multiple of market price that products would have to be sold at for the plant to break-even over its lifetime. This is presented as the ratio of TAC to revenue earned from selling the products (which can be either the alcohols for the C2A case, or olefins in the C2O case):

$$GP = \frac{TAC}{REV} \quad (5.11)$$

The effect of varying market prices and raw material costs on the GP for both C2A and C2O plants was also investigated. First, the uncertainty distributions for TCI, H₂ and CO₂ were split into 10 discrete bins, each with a given probability and value. Taking the Cartesian product of these uncertain costs and the 313 weekly market prices for methanol, ethanol, olefins, electricity and natural gas gave 313,000 different potential market scenarios, each with their own probability of occurring (313 weekly market prices multiplied by 10³). The GP for each of the C2A and C2O routes could then be calculated in each of these scenarios, allowing a more robust comparison in the economic performance between each route.

CH₄ Formation Adjustments

As previously mentioned, CH₄ formation is relatively high for Catalyst G, with certain reaction schemes and conditions leading to per-pass selectivities toward CH₄ above 80%. This undesirable high rate of generation is likely to be detrimental to the profitability of the scaled-up process, and as such, various measures were identified and investigated to mitigate this (i.e. increasing purge rates and including a RWGS or TRM pre-reactor). However, as this is an early-stage assessment of the catalyst and technology, it is beneficial to investigate directly the effect of CH₄ selectivity on the GP of the overall C2O value chain, and provide potential targets for future catalyst development.

To investigate this, adjustments were made to the CH₄ per-pass selectivity for the Catalyst G reaction schemes, where reductions of 50, 75, 90, 95 and 99% for each scheme were made relative to their baseline selectivity. The adjustments were made by taking the balanced outlet molar flows calculated by optimisation problem 5.1, and reducing the outlet flow of CH₄ by the desired percentage. It was assumed in these adjusted reaction schemes that all CH₄ was formed from the methanation reaction:



And as such, the amounts of water formed were also adjusted, as well as the consumed CO and H₂ to account for the reduced CH₄ formation. This is the conservative approach to changes in reaction selectivity, as it has the parallel effect of reducing the overall per-pass conversion rate. For each reaction scheme and potential selectivity reduction, the new per-pass CH₄ selectivity was calculated, and the C2A and C2O simulations and GP market scenario analysis were repeated for the G-BC route using each of these new reduced versions of the reaction schemes. This allowed the direct effect of reducing CH₄ selectivity to be determined.

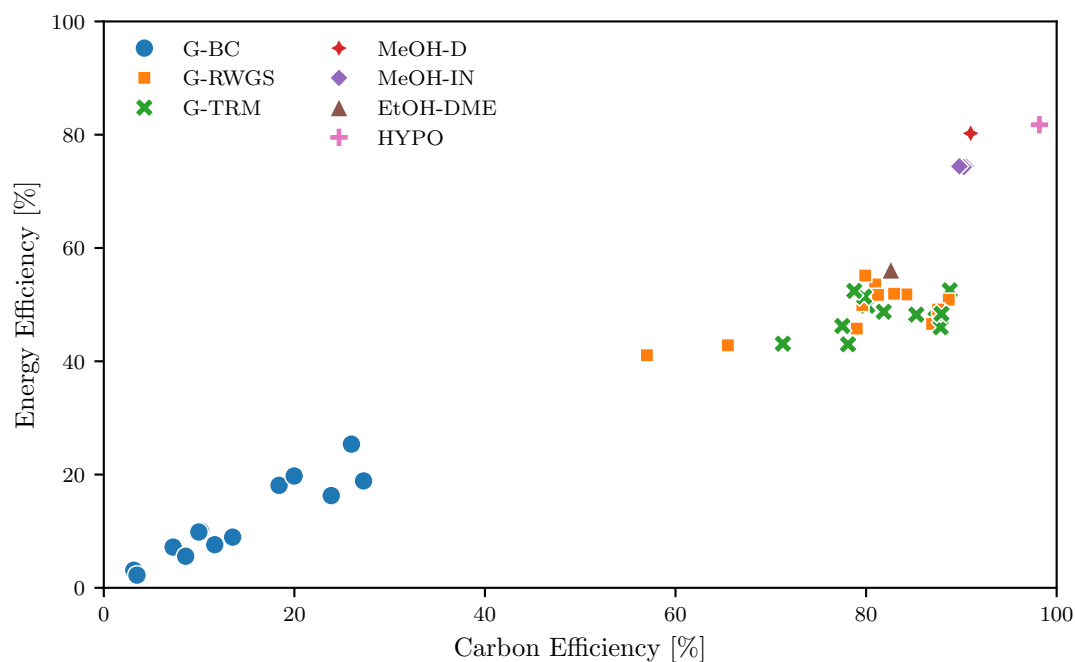


Figure 5.5: Carbon and energy efficiency of the C2A routes.

5.3 Results

5.3.1 Efficiency

Figure 5.5 shows the carbon and energy efficiency for all of the considered C2A plants. Multiple points are shown for the Catalyst G routes, and the indirect MeOH route as they represent different reaction conditions and the different pre-reactor pressure levels. The first result that can be garnered from this figure is that the G-BC is simply not competitive. The highest carbon and energy efficiency achieved for all G-BC routes are only 27 and 25% respectively. This is due to the large formation rates of CH₄ in the base case, which leads to a large required purge rate to prevent build up beyond 10% in the reactor feed. In fact, the lowest purge rate out of the potential G-BC routes was 6%, which is significantly higher than what is used for MeOH-D route at 1% (Pérez-Fortes et al., 2016).

Significant improvements in carbon efficiency are achieved with the addition of the pre-reactors for the Catalyst G routes, with G-RWGS and G-TRM both exhibiting efficiencies up to 89%. Converting the CH₄ into additional syngas allows the purge rate to be reduced down to the same 1% value as the MeOH-D route, leading to a significantly

higher overall carbon efficiency. The energy efficiency also improves up to 53% for these routes. Interestingly, the energy efficiency of both the G-TRM and G-RWGS routes are comparable, which confirms the trade-off between the high external heating demand for the endothermic RWGS reactor, and the increased compression duties due to additional O_2 fed in the G-TRM option.

Both the G-RWGS and G-TRM options are similar in carbon and energy efficiency to the EtOH-DME route, which has a slightly higher energy efficiency at 56%, but a slightly lower carbon efficiency than the best performing G-RWGS/G-TRM routes at 83%. The slightly higher energy efficiency is due to the lack of a large recycle in the compression train at the feed section, however the multiple reaction sections with imperfect selectivity and separation cause an accumulated effect in carbon losses from the desired ethanol end product.

However, there are significant gains in energy efficiency for both MeOH-D and MeOH-IN routes when compared to G-RWGS and G-TRM (approximately 74% for indirect and 80% for the direct route). A higher per-pass conversion in the reactor bed leads to lower recycle rates in both of these routes, with per-pass conversions approaching equilibrium at 27% for the MeOH-D route, and 77% for the MeOH-IN route. The per-pass conversions for the highest Catalyst G routes, by comparison, are only 14% for the G-BC routes, and 27% for the G-RWGS/G-TRM routes. For the MeOH-IN option, this increased per-pass conversion mainly leads to lower recompression duties and therefore lower electricity consumption in the feed section. For the MeOH-D route, the smaller gaseous reactor recycle is also kept at elevated pressure, removing the lack for significant recompression duties and reducing electricity consumption even further. This suggests that it may be beneficial to operate the Catalyst G reactor at lower GHSV values in an attempt to increase the per-pass conversion. This will likely change the product distribution and should therefore be investigated experimentally, and it will also lead to greater catalyst costs, but it may be a worthwhile trade-off to reduce the recycle rates in the reactor section.

Finally, there is the HYPO route, which has the highest carbon efficiency at 98%,

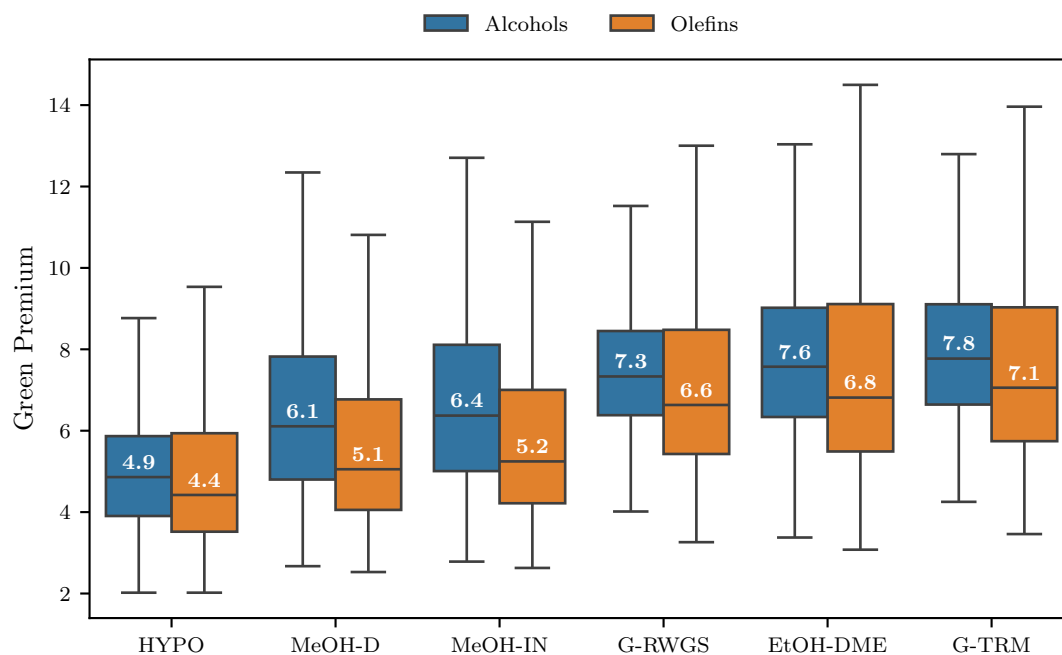


Figure 5.6: Green premium distributions for alcohol and olefin production for the best performing version of each route type. Box plots show the distribution of green premiums across varying market scenarios (low, average, and high price cases), with median values highlighted. These ranges represent economic scenario uncertainty rather than measurement error.

and the highest energy efficiency at 82%. As this acts as a theoretical upper bound for direct production of CO₂-to-Ethanol, this likely isn't achievable in practice, but it confirms that there is no inherent trade-off in producing ethanol versus methanol from an efficiency point-of-view.

The main conclusion that can be taken from this set of results is that the C₄ formation severely limits the performance of a scaled up Catalyst G plant. The addition of the pre-reactors that convert the CH₄ help in terms of carbon efficiency, but the energy efficiency is still low especially when compared to methanol synthesis. An initial target for catalyst development should therefore be to focus on reducing the CH₄ formation rate. There also may be a benefit with operating at a lower GHSV i.e. using more catalyst within the reactor bed, which may increase per-pass-conversion enough to offset the increase in catalyst costs.

5.3.2 Green Premium

Figure 5.6 shows the range of green premiums for each C2A route, both for alcohol production, and when 10 plants are used to feed a centralised olefins manufacturing facility. The box plot distributions take into account the varying market scenarios as described in Section 5.2.4. Note that since there are multiple versions of each C2A route, only the version with the lowest GP values are shown here to represent the performance of the overall route.

The first important point is that G-BC is now shown, as its GP's are significantly higher than the other routes at 18.3 for alcohol production, and 15.6 for olefins production. Please refer to Figure C.2 in the appendices for a version of Figure 5.6 with G-BC shown. As revealed by the carbon efficiency results, the carbon losses are too significant for the G-BC routes, and thus the quantity of alcohol products (and thus olefins) manufactured are too low to be profitable.

For the other routes, whilst there is significant overlap in the in the GP distributions, an overall trend can be distinguished from the median results and inter quartile ranges (IQR). The HYPO route has the lowest GP at 4.9 for alcohols and 4.4 for olefins, which is unsurprising considering its very high carbon efficiency. Both the methanol routes are second and third in terms of GP, and have a very similar performance, with only a 4-5% increase in GP for MeOH-IN over MeOH-D, at 6.4 and 6.1 for alcohols, and 5.2 and 5.1 for olefins. This is mainly due to the lower compressor duties and lack of RWGS reactor in the MeOH-D route, which both lead to a lower capital investment.

G-RWGS is the best performing Catalyst G route, with a GP of 7.3 for alcohol production and 6.6 for olefins production. Whilst this is a significant increase over the market prices for both alcohols and olefins, this is only a 15-26% increase in GP when compared to the MeOH-IN route, which is the most similar in overall plant configuration. The G-RWGS is also slightly lower in median compared to the EtOH-DME route, however, there is only a 2-3% difference between the two, which is well within the margin of error. The G-TRM route is only slightly higher than both with GPs at 7.8 and 7.1 for alcohols and olefins respectively.

Although there is significant overlap between the IQRs of the different routes, a general trend that is consistent across all route families is the decrease in GP when moving from alcohol production to further downstream olefin production. This illustrates the absorption of increased feedstock costs as the material is converted and upgraded through a value chain. Typically for green chemicals, it is the increased feedstock costs that drive the higher price over their fossil-fuel based alternatives. However, as the number of steps increases through a value/supply chain, these initial feedstock costs become a smaller and smaller proportion of the overall cost of production. Parallel to this, the inherent value of the produced product increases through a value chain, which in theory leads to increased profitability. This is corroborated by work performed by Tonny Manalal et al. (2025), who demonstrated this effect in a chemical cluster with feedstock switches to CO₂ and biomass. A downside of moving to further olefin production is the larger variability in market price, which is illustrated with the larger overall range and greater minimum/maximum potential GPs for the C2O route. However, this increased variability can likely not be generalised across other value chains as it will be heavily dependant on regional demand and supply.

5.3.3 C2O Value Chain Cost

Figure 5.7 shows the total annualised cost and revenue for each type of C2O value chain. Note that these results were obtained using the average market pricing scenario for both the procurement of raw materials, utilities, CAPEX etc., as well as the revenue earned from the sale of the final olefin products. These results are also for the separate dehydration case in the centralised olefins plant. It is clear that the cost of the C2A plants dominate the overall cost across all route families, contributing 94-98% of the TAC, with the 2-6% remaining coming from the centralised olefins facility i.e. the MTO and ETE plants.

Specifically, it is the cost of green H₄ that is the greatest proportion of overall cost in the C2O value chain, from 56-77% of the total cost across the route families. This finding also implies that there is little benefit in increasing the capacity of the C2A plants (or

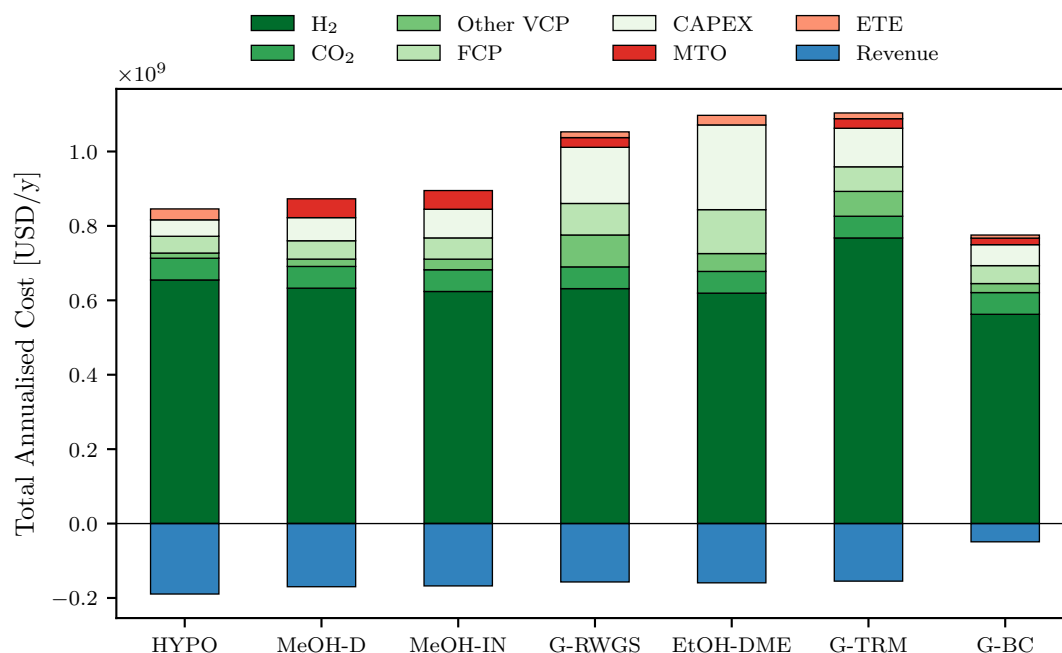


Figure 5.7: Total annualised cost breakdown for C2O value chain per route family for 10 connected C2A plants. Green bars represent costs for C2A plants, orange/red represent costs for a centralised separate-dehydration olefins plant.

increasing the number of C2A plants in the C2O value chain) and realising economies of scale benefits as the H₂ increases linearly with capacity. The high cost of green H₂ also confirms why there is a negligible difference between the separate and co-fed GP results for the C2O value chain, with less than 1% difference between the two options for G-RWGS and G-TRM (please refer to Figure C.3 in the appendices).

Investigating the TAC breakdown for each route specifically, the G-BC route has the lowest overall value chain costs at 775m USD/y. In contrast to the GP results above, the high purge rate for this route aids in maintaining a low TAC by reducing the amount of CO_x recycled to the reactor, and thus reducing the overall H₂ demand and cost for conversion. However, the high purge rate results in a significantly reduced alcohol (and therefore olefin) production rate, and leads to a significantly smaller revenue than the rest of the routes at 49m USD/y on average, which results in the larger observed GP values.

The HYPO route has the second lowest TAC as well as the highest overall revenue, at 846m and 189m USD/y, respectively. It's closely followed by both of the methanol routes, which have similar TACs at around 880m USD/y, with minor increases in utility,

capital and fixed costs for the MeOH-IN route over the MeOH-D route. Again, this increase in costs for the MeOH-IN route over the MeOH-D route can be explained by the additional RWGS reactor, and higher compression duties and requirements of the indirect route. These routes also have slightly lower revenues than the HYPO route at 168m USD/y on average. Comparing the cost breakdown between the HYPO and MeOH routes reveals one advantage of ethanol as a feedstock over methanol when considering olefins production: the total annualised cost of an ETE plant is lower than an MTO plant at a similar scale (29m vs 50m USD/y). The higher selectivity and reduced number of side-products in the ETE plant compared to the MTO plant significantly simplifies the separation section, and leads to both reduced capital investment and utility requirements. However, to reiterate, this decrease in cost is minor compared to the overall cost of the C2O value chain with green H₂ as a feedstock.

Analysing the TAC breakdown for the remaining routes reveals a significant increase in cost for EtOH-DME, G-RWGS, and G-TRM over the MeOH routes. The EtOH-DME route has the second highest value chain costs out of all routes, at 1.10bn USD/y, and it has a significant annualised CAPEX component at 230m USD/y, which is also the highest amongst all of the C2A routes. This is unsurprising, given that the route involves several different reaction and separation sections, and very large recycle rates, specifically within the DME hydrocarbonylation section where a very high CO:DME ratio (in the order of 20:1) is required to achieve a high conversion rate (Cheung et al., 2007). This increases the required capacity of all equipment within this recycle loop, but also leads to a substantial required heat exchange network area, driving the capital costs up further. Comparing the final two Catalyst G routes, the G-TRM option has very similar costs than EtOH-DME, which are slightly higher than the G-RWGS route, at 1.10bn and 1.05bn USD/y respectively. Although the G-TRM route has a lower capital requirement, due to a smaller heat exchange network (as the high heat requirement for the endothermic RWGS reactor has been mitigated), its H₂ requirement is 22% higher on average. This is due to the additional O₂ feed, which increases the conversion of CH₄ in the pre-reactor, and thus leads to a higher CO_x recycle rates to the reactor, and thus

a higher H_2 requirement. Since all three of these routes have a similar carbon efficiency in the C2A plants, the overall revenues for their C2O value chains are comparable at approximately 156m USD/y.

These results also reveal the main area where the Catalyst-G routes lose cost competitiveness compared to the methanol and HYPO routes. In general, G-RWGS and G-TRM have higher recycle rates and recompression duties, which significantly increase the utility and capital costs of the plants, as shown by the Other VCP (which is primarily utility costs) and CAPEX bars. The FCP bar is also related to the capital cost, as the correlations and method used to determine is use the CAPEX as a basis. When combined with the fact that the G-BC route has low and similar capital costs to the methanol and HYPO routes, it further implies that if CH_4 formation rates are reduced, the pre-reactors and recompression of the reactor recycle will no longer be required and Catalyst G could become more competitive.

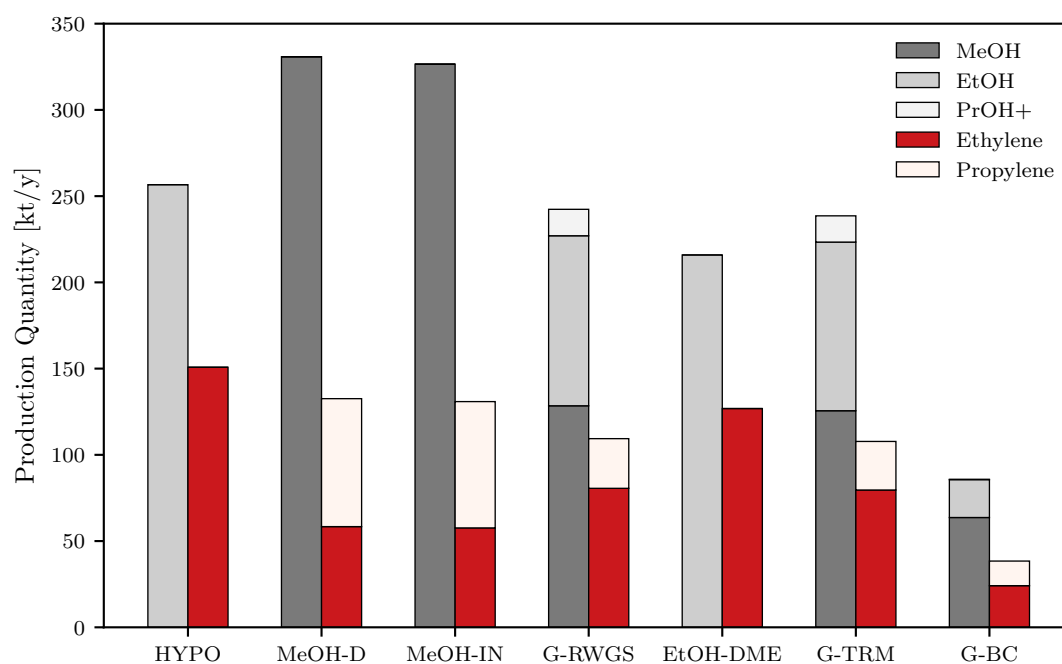


Figure 5.8: Alcohol and olefin product distributions for each C2O value chain.

Although these results in general indicate that there is little-to-no economic benefit in producing ethanol in one step compared to the indirect EtOH-DME, it is promising that there isn't a significant penalty for doing so with the current catalyst performance. Since the context of the work concerns surfactant manufacture, and therefore only ethylene

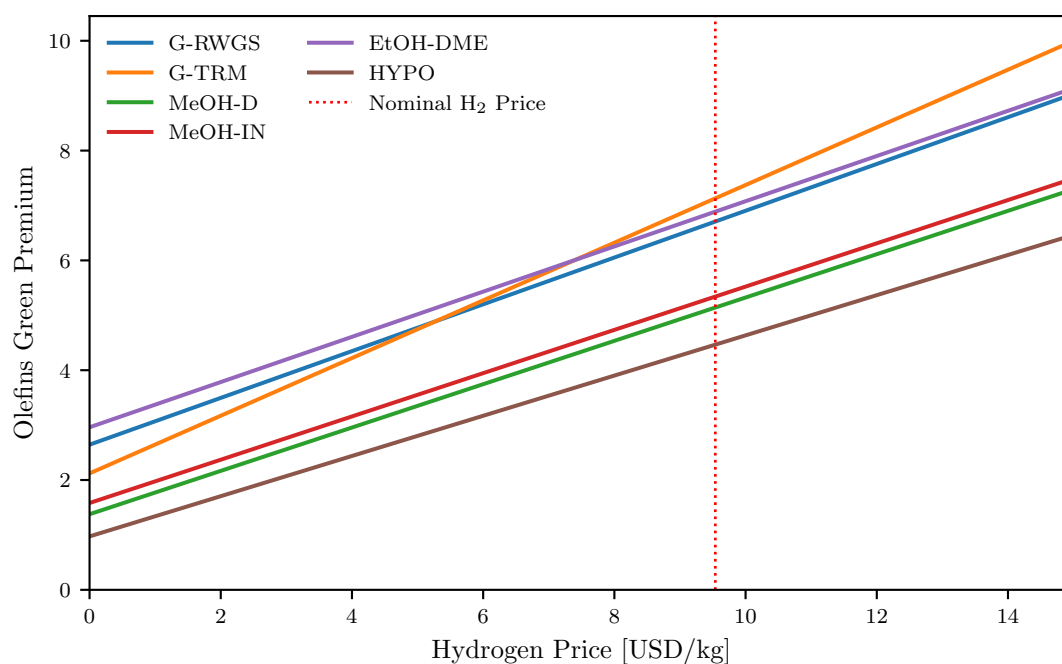


Figure 5.9: Sensitivity analysis of the olefins GP for each C2O value chain with respect to H₂ price. Average prices used for CAPEX, market prices and CO₂ costs.

is the desired end olefin product, the Catalyst G routes could be more competitive in scenarios where an MTO based route leads to the oversupply of propylene. Expanding on this, Figure 5.8 shows the production quantities for both the alcohol and olefin products for each C2O value chain. Although the MeOH routes had the lowest overall GPs (excluding the HYPO route) they have the second lowest ethylene production quantity, at 58 kt/y. The G-BC route is still the lowest with only 24 kt/y produced, but both G-RWGS and G-TRM produce 38% more ethylene than the MeOH routes, at 80 kt/y. However, the EtOH-DME route's ethylene production rate is higher still, at 126 kt/y. Whilst this result still argues that the EtOH-DME performs better over a single-step CO₂ to ethanol catalyst, there may be scenarios where the lower capital costs associated with the single-step route (especially at smaller CO₂ feed rates), would be preferable.

H₂ Sensitivity

Following on from the dominant H₂ costs in Figure 5.7, a sensitivity analysis was performed on each C2O value chain, varying the cost of H₂ whilst maintaining the rest of the prices and economic parameters at the average scenario. The results of this sensitivity

analysis are shown in Figure 5.9.

The HYPO and MeOH routes both have similar H_2 requirements and therefore exhibit the same sensitivity towards the H_2 price. However, at a green H_2 price of 3 USD/kg, which is predicted to be an achievable global average price by 2050 (Frieden and Leker, 2024; IEA, 2020), these routes approach an average olefins GP of 2-2.7, which is a 47-55% reduction over the current nominal price scenario.

In the other routes, G-TRM has the highest overall H_2 demand, and therefore the highest H_2 sensitivity. At the nominal price of 9.6 USD/kg, it is the most expensive route on average at a GP of 7.1. But if the price of H_2 drops to 7.5 USD/kg, it becomes competitive with the EtOH-DME route at a GP of 6.0, and a further reduction to 5.3 USD/kg leads it to becoming cheaper than the G-RWGS option at a GP of 4.9. At the 2050 predicted average H_2 price of 3 USD/kg, the G-TRM reaches a GP of 3.7, which is 12% lower than the EtOH-DME route at a GP of 4.2. However, this is still 37-85% higher than the GPs of the HYPO and MeOH routes.

Investigating further with the extreme case of free green H_2 production (for example, from excess renewable electricity generation that would otherwise have to be curtailed (Al-Ghussain et al., 2022)), only the HYPO route becomes competitive with fossil-fuel based olefins production i.e. a GP of 1. Both of the methanol routes are close, at 1.3 and 1.6 for MeOH-D and MeOH-IN respectively. However, the G-TRM route as the lowest catalyst G route manages an absolute minimum GP of 2.1 in this instance. As these periods of free green H_2 are likely to be rare and infrequent, it can be concluded that there is no H_2 pricing scenario where the catalyst G routes will be competitive with methanol synthesis at their current level of performance. However, by the predicted 2050 prices,

5.3.4 Effect of Methane Reduction

Figure 5.10 shows the effect of reducing the selectivity of Catalyst G towards CH_4 production on the overall C2O value chain GP. The 0% values refer to the baseline per-pass selectivity i.e. the current performance level of each of the reaction schemes for Catalyst

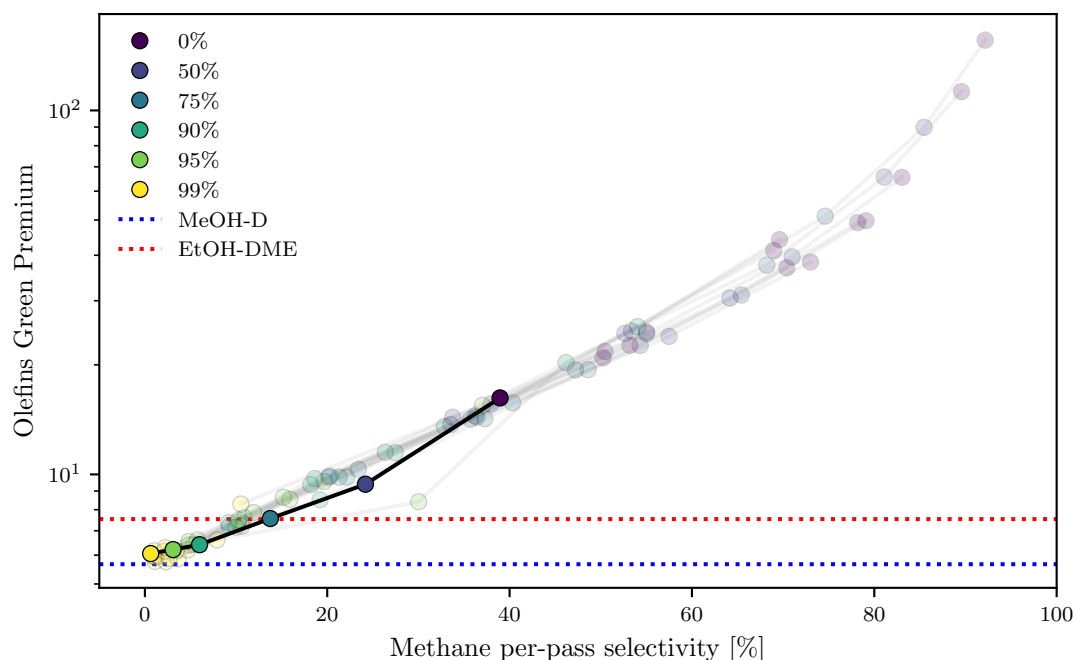


Figure 5.10: Effect of reducing Catalyst G CH₄ per-pass selectivity on G-BC C₂O value chain green premium. Colour scale indicates relative reduction in selectivity compared to experimental data. Best performing G-BC reaction scheme highlighted.

G, whereas the other percentage reduction values are explained in Section 5.2.4. As is shown in Figure 5.10, some of the base case routes have GPs greater than 100, and correspond to a very high per-pass selectivity towards CH₄, with values greater than 80%. The reaction scheme with the lowest per-pass selectivity towards CH₄ (and the lowest GP of the G-BC routes) still only achieves a GP of 15.6 (as shown in the appendix box plots), and a per-pass selectivity of 39% towards CH₄. With a 50% reduction in CH₄ formation rates, there is only a 40% reduction in GP for the best performing route, and most reaction schemes still have GPs greater than 14. With reductions between 75-90% over the baseline, many of the routes now have GPs close to 10, and correspond to a per-pass selectivity of 20%. However, to be competitive with the EtOH-DME route would require per-pass selectivities of approximately 10% towards CH₄, which corresponds to a 90-99% reduction in the current catalyst selectivity. Going further, an almost complete reduction in CH₄ selectivity i.e. the 99% investigated in this work, leads to per-pass selectivities less than 10% and will lead to catalyst G becoming competitive with the MeOH-D route.

Overall, this highlights the difficulty in converting CO₂ to ethanol with a single catalyst. Without the RWGS or TRM pre-reactors to convert the undesired CH₄ formed on

the Catalyst G bed, targeting a per-pass selectivity of 10% when the current best performing reaction conditions could only manage a 39% selectivity is a substantial challenge for catalyst development.

5.4 Conclusions

This chapter investigated the scaled-up techno-economic performance of a novel catalyst (Catalyst G) that aimed to convert CO_2 to ethanol in a single step, with the aim of further ethylene production via dehydration for downstream surfactant manufacture. Experimental data and yields from various reaction conditions were used to create 18 different reaction schemes that formed the basis for Aspen HYSYS models. Three variations of the Catalyst G model were created: a base case, and two with either a reverse-water-gas-shift or tri-reforming of methane pre-reactor to convert the unwanted CH_4 side product. Four other CO_2 -to-Alcohol (C2A) routes were modelled as comparisons: a hypothetical CO_2 -to-Ethanol route with 100% selectivity, two methanol synthesis routes, and an indirect ethanol route via dimethyl-ether hydrocarbonylation. The analysis also investigated the economic performance of connecting multiple C2A plants to a centralised olefin production facility.

The efficiency results revealed that the base case carbon efficiency could only reach a maximum of 27% due to the large CH_4 formation rates, and subsequent high purge rates to prevent its build up within the reactor feed. This corresponded to a green premium that was significantly higher than the other investigated routes (18.3 for alcohol production, and 15.6 for olefins production). Adding the RWGS or TRM pre-reactor significantly improved the carbon and energy efficiency to 89% and 53%, respectively, and thus also improved the green premium, which dropped down to 7.3-7.8 and 6.6-7.1 for alcohols and olefins, respectively. This made Catalyst G competitive with the indirect ethanol route, but both were lower in terms of energy and carbon efficiency, and green premium compared to the hypothetical and methanol routes. The latter achieved green premiums as low as 6.1 for alcohol production and 5.1 for olefin production.

The economic analysis revealed that the green H₂ feed was the primary driver for the high GP values across all routes, contributing between 56-77% of the overall olefin value chain costs. This also demonstrated that there are limited opportunities for taking advantage of economies of scale in both the alcohol or olefins plants, and also no benefit in co-fed dehydration at the olefin facility. A further sensitivity analysis confirmed that although the predicted 2050 prices would substantially reduce the green premium for all routes, there is unlikely to be a pricing scenario where the catalyst G routes are competitive with methanol synthesis. However, in the cases where there is limited-to-no propylene demand, routes where a greater proportion of ethylene are formed at the olefin facility i.e. routes that manufacture more ethanol from the alcohol plant, could become more favourable.

Finally, an investigation into the effect of methane formation reduction was performed. This revealed that the current catalyst can achieve a minimum per-pass selectivity of approximately 39%, but would need to reduce this to 10% in order to become competitive with methanol synthesis. This corresponds to a 90-99% reduction in the current CH₄ formation rates, which is a substantial improvement target for future catalyst development.

The priority in future work is to determine if there exists market scenarios where the oversupply of propylene would make a CO₂ to ethanol catalyst more competitive with methanol-mediated ethylene production, and perform further economic assessments in these scenarios to determine if Catalyst G with either a TRM or RWGS reactor could become competitive. Additionally, catalyst development should focus on minimising the methane formation rates whilst maintaining a high ethanol selectivity.

Chapter 6

Methane Side Stream Valorisation

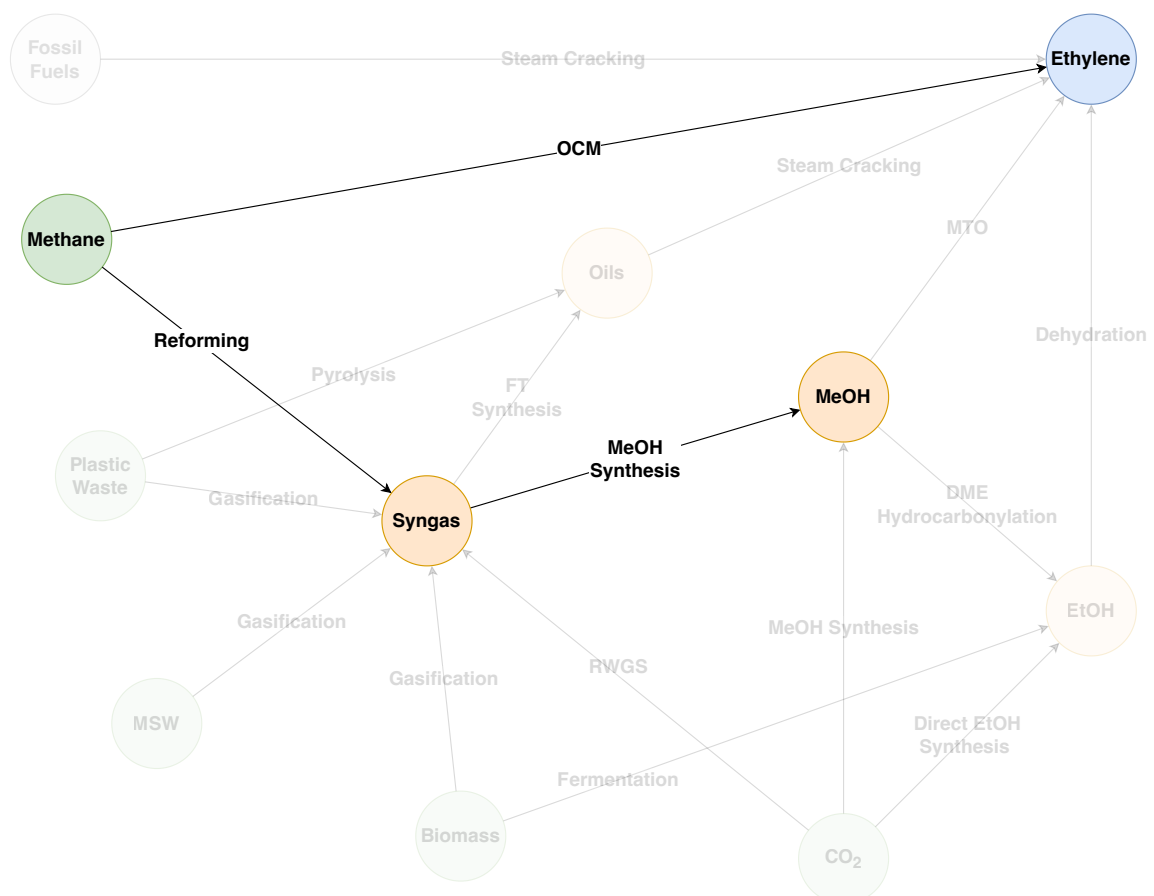


Figure 6.1: Overview of production routes assessed in Chapter 6.

6.1 Introduction

Methane is a by-product of many different chemical processes, including steam cracking for the production of olefins, pyrolysis and gasification processes, aromatic dealkylation and the anaerobic digestion of wastewater sludge (Lange, 2021). The most common use of these methane side streams is as a fuel, where it is combusted to either directly provide process heat or to produce additional electricity for the base plant in a turbine. This use of methane helps chemical plants to close their energy balance and aids in their profitability by reducing their requirement for external energy sources (Zimmermann and Walzl, 2009). Furthermore, in the oil and gas sector, any excess methane recovered during operations is simply flared when recovery proves uneconomical.

However, more recently the chemical industry is striving towards a more sustainable future, and the combustion of these methane side streams is increasingly becoming at odds with these goals. Each kilogram of methane emits approximately 2.75 kilograms of CO₂ after undergoing complete combustion, which represents a substantial carbon footprint that is becoming harder to justify as decarbonisation targets continue to tighten. Not only does the combustion of methane contribute to climate change directly, but methane itself is a potent greenhouse gas, with a global warming potential approximately 30 times greater than that of CO₂ (Intergovernmental Panel On Climate Change, 2023a). Incomplete combustion or leaks of methane from the system can therefore exacerbate the environmental issues further, and it has even been discovered that flaring in oil and gas operations is less efficient than previously believed for the conversion of excess methane (Plant et al., 2022). In response to these pressures, the chemical industry is actively pursuing alternatives to methane combustion. Fuel-switching represents one of the most common strategies, where the methane and other fuels combusted in a chemical process are swapped for biomass, hydrogen, or electricity via electrification (Sunny et al., 2022). However, if fuel switching is performed, a key question remains: how can the methane side stream now be valorised? Following the principles of the circular economy, where materials should be kept at their highest level of value (Ellen Macarthur Foundation, 2019b), this methane could instead be used as a feedstock to produce additional valuable

chemicals. Not only does this avoid the direct emissions from combustion, but it would potentially still aid in the base plant's profitability with the additional revenue from a new chemical product.

The most common alternative use for methane is for the manufacture of H_2 via steam methane reforming, which is the route used to produce over half of the world's H_2 (Iulianelli et al., 2016). Whilst this is an attractive option, these plants typically have to operate at very large scales in order to be profitable (Schüth, 2019) and it still requires the capture and storage of the CO_2 in order to reduce its global warming emissions. An alternative product that could be targeted from methane reforming is instead methanol via syngas. As discussed in Chapter 2, methanol is predicted to become a key platform chemical in the future chemical industry. Additionally, steam reforming of methane could be replaced with a more novel reforming approach called tri-reforming of methane (TRM). Tri-reforming presents an attractive option by combining steam reforming, dry reforming, and partial oxidation in a single process (Song and Pan, 2004). This integration can enable autothermal operation, significantly reducing operating expenses compared to conventional reforming. The process can produce syngas with a $H_2:CO$ ratio approaching the optimal 2:1 ratio required for methanol synthesis, whilst the inclusion of CO_2 as one of the reactants aligns with carbon utilisation goals (Alli et al., 2023). Whilst there is a lack of commercial experience in deploying TRM as the development of a stable catalyst is still ongoing, its synergistic effects make it appear to be a promising alternative to other reforming routes (Pham Minh et al., 2018).

An alternative to the indirect valorisation of methane via syngas is oxidative coupling of methane, where it reacts with oxygen to form ethylene in a single step. As introduced in Chapter 2, despite decades of research, OCM catalysts still struggle with low selectivities and yields towards ethylene (Cruellas et al., 2019). However, the promise of single-step ethylene production may make OCM a more suitable route for smaller scale methane flowrates, as could be the case for smaller fuel-switched chemical plants.

The aim of this chapter is to assess the enviro-economic performance of both TRM and OCM as an option for valorising a methane side stream from a chemical plant that

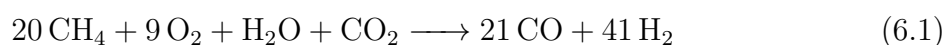
has undergone fuel-switching, specifically electrification with renewable electricity. These routes are compared to the case where electrification has not taken place, and the methane side-stream continues to be combusted for energy. Various methane flowrates are considered to determine at what scale these routes could be cost-competitive with the base case, and an economic feasibility study is performed to assess under what market conditions these routes could become profitable overall. Finally, the global warming potential was calculated for both routes to confirm if there is an environmental benefit when converting methane side streams into additional chemicals.

6.2 Methodology

Both the TRM and OCM routes were modelled using Aspen HYSYS V14. The CH₄ feed flowrate was varied from 2t/h up to 64 t/h to consider a range of possible capacities, where the 64t/h upper bound is based on the CH₄ side-stream flowrate from a world-scale naphtha steam cracker (Lange, 2021). The property packages used for both models were NRTL at pressures less than 10 bar, and RKSMHV2 for pressures greater than 10 bar. The OCM route also used the Peng-Robinson equation of state in its separation section described below.

6.2.1 Tri-Reforming of Methane

Figure 6.2 shows a diagram of the TRM process. First, the CH₄ feed is mixed with the other reactants (water, O₂ and CO₂) and heated up to the reaction temperature of 950°C (Graciano et al., 2018). The mixture is then fed to the reforming reactor, which was modelled using a Gibb’s equilibrium reactor in HYSYS (R-100). Note that when choosing the ratio of reactants, the following global reaction stoichiometry was used (Arora and Prasad, 2016):



This stoichiometry leads to almost autothermal operation i.e. enthalpy of reaction

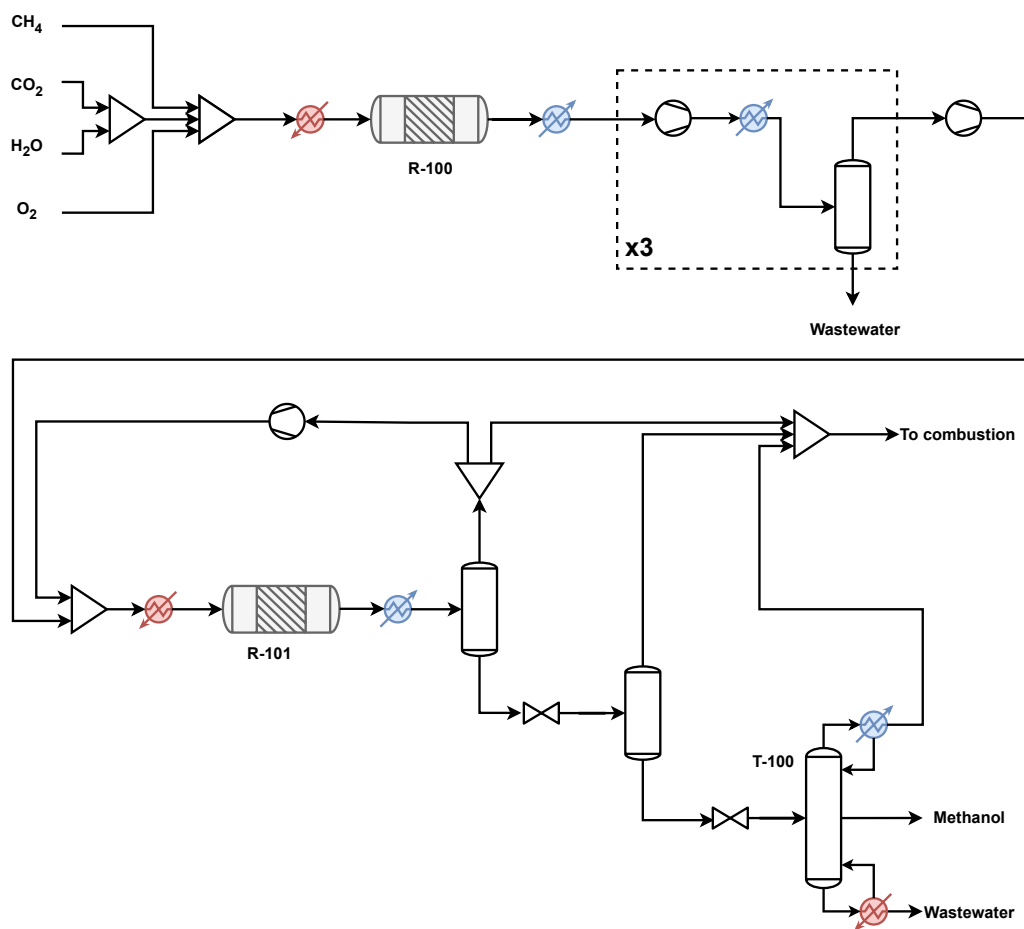


Figure 6.2: Process flow diagram of tri-reforming of methane route coupled with methanol synthesis.

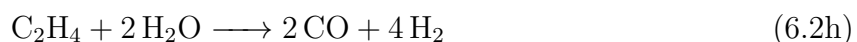
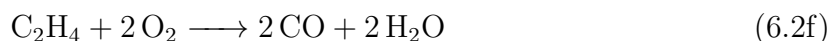
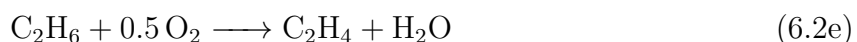
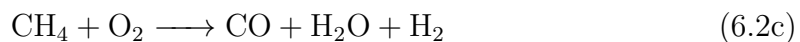
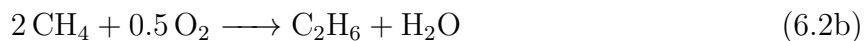
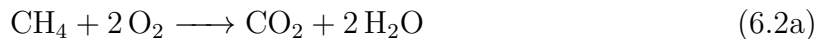
close to zero, and also produces syngas close to the desired 2:1 H₂:CO ratio for methanol synthesis. The products consist of CO, H₂, water, some CO₂ and unreacted CH₄, and are cooled after exiting the reforming reactor and sent towards the methanol synthesis section. This methanol section is described previously in Chapter 4.

6.2.2 Oxidative Coupling of Methane

Reaction Kinetics

The basis for this process is the kinetic model developed by Stansch et al. (1997), which is the most frequently used kinetic model in OCM simulation work (Da Ros et al., 2021),

and is comprised of the following 10 reactions:



Whilst there are more recent kinetic models for OCM catalysts (Pirro et al., 2021), these are predominantly microkinetic in nature and not possible to define directly in Aspen HYSYS. For simplicity, the global reaction scheme was used. An issue with this reaction scheme is that some of the reaction rate equations do not depend on the partial pressure of O_2 . This means that when O_2 is completely consumed, some of these reactions continue at an accelerated rate when the overall reaction system should halt. Therefore, the reactor was sized to stop when either O_2 was completely consumed, or when a maximum temperature was reached (955 °C); both for safety reasons to prevent an exothermic runaway reaction, and as the upper bound for validity of the kinetics. However, implementing this reactor sizing mechanism using an adjust block in HYSYS leads to severe difficulty in convergence. If the adjust solver overshoots its volume adjustment for the PFR until after O_2 has been completely consumed, it lacks gradient information on the O_2 concentration to infer the direction for its next iteration, and can therefore get trapped in this zero-gradient region.

To circumvent this, the rate equations for reactions 6.2 were implemented as an ODE system in Python. The steps for solving the reaction system were then as follows:

- Design the ODE system of reactions, calling the relevant HYSYS fluid package to calculate the heat capacities of the reactor stream/mixture. This ensures the adiabatic temperature change from the reaction matches the results that would be generated in HYSYS.
- Use HysysPy to export the feed information for the reactor into Python.
- Solve the molar flowrate ODE system until one of the terminal conditions is reached.
- Export the resulting flowrates from solving the ODE system back to HYSYS as the product stream, which is then connected to other subsequent unit operations.

Some additional metrics for the reactor were also calculated in Python, and exported into a spreadsheet object in the HYSYS simulation, which included volume of reactor, mass of catalyst and CH_4 conversion. Note that since there is no longer an official connection between the feed and product streams of the reactor in HYSYS, recycle blocks can no longer use convergence acceleration methods, such as the default Wegstein method for recycles (Wegstein, 1958). A direct substitution alternative was therefore implemented in Python. Even though recycle acceleration is lost with this method, in preliminary testing, the solve time caused by an increase in iterations was negligible compared to the issues with the build-in adjust block iterating within a recycle loop.

Process Description

Figure 6.3 shows a diagram of the OCM process. The flowsheet begins with CH_4 feed mixing with O_2 at a desired ratio. The selection of O_2 feed ratio has a strong impact on the overall conversion and selectivity of the system towards ethylene. Based on work performed by Penteado et al. (2018), a 10:1 CH_4 : O_2 ratio was chosen to maximise selectivity towards ethylene at the expense of a greater per-pass conversion. The feed mixture is heated to 700°C where it is fed to the first OCM reactor R-100 (i.e. the Python import/export reactor implementation). The products are then cooled back down to 700°C ,

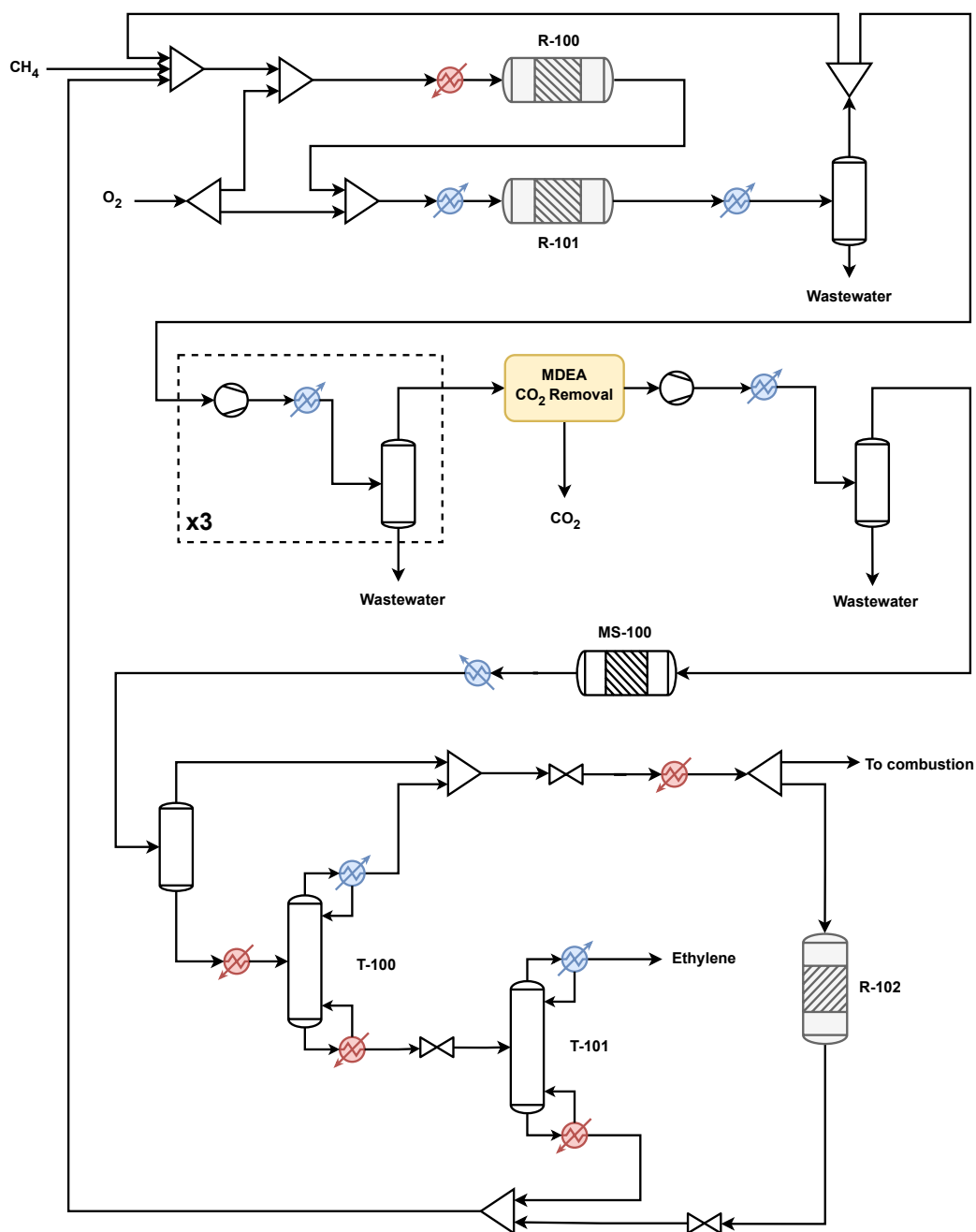


Figure 6.3: Process flow diagram of oxidative coupling of methane route for ethylene production.

and additional O₂ dosing is used to bring the ratio back to 10:1, before being fed to a second OCM reactor (R-101). The products from the second reactor are then cooled and a flash vessel is used to remove some of the condensed water. The per-pass conversion of

this system is low, so in order to reduce recycle rates from the separation section, 50% of the gaseous product mixture is recycled back to the start of the reactor section.

After the reaction section, the product mixture, which consists mainly of unreacted CH₄, ethylene, ethane, water, CO₂ and light gases, is sent to a compression train and separation section. These following sections are similar to those seen in olefins production facilities (Zimmermann and Walzl, 2009). The compression train consists of 4 stages with interstage cooling and flash vessels to remove condensed water from the stream. After the third stage, an MDEA based CO₂ removal section is used to allow polymer grade ethylene to be recovered further downstream. It is assumed that this forms part of a CCS system, and the removed CO₂ is sent to geological storage (Terlouw et al., 2021a). After the fourth compression stage, the product stream reaches 40 bar and is sent through a molecular sieve dryer (MS-100) to remove any final traces of water from the stream.

Next, the remaining gaseous products are cooled to -94°C and then flashed to remove bulk of the light gases (i.e. H₂, CO and some CH₄). The liquid from the flash is then sent to a demethaniser column (T-100), where any remaining CH₄ is separated from the tops and the C2 components are recovered from the bottom. The CH₄ and lights streams are mixed, and heated to 325°C before passing to a methanator reactor (R-102). This reactor converts the H₂ and CO side products back into CH₄, so they can be recycled to the start of the process:



The kinetics from Hou and Hughes (2001) were used to implement this reactor as a PFR in HYSYS. This methanator is critical to obtain a higher carbon efficiency and overall ethylene production rate for this process. A small purge is used to prevent the build up of inert species from the process.

Finally, the C2 stream from the bottom of the demethaniser is reduced to 19 bar and then sent to a C2 splitter column (T-101), where polymer grade ethylene is recovered from the top at a purity of 99.96 mol%, and ethane is recovered from the bottom. The ethane is another intermediate that can be directly recycled back to the reaction section.

6.2.3 Route Assessment

HysysPy was used to solve each route at each CH_4 flowrate, and extract the relevant process information to perform two separate assessments: a techno-economic analysis, and life cycle assessment to determine the global warming potential. Additionally, HysysPy was used to extract process-level KPIs included carbon efficiency (i.e. the percentage of carbon atoms in the CH_4 feed that end up in the methanol or ethylene product), product production rates, and utility requirements for the routes.

Techno-Economic Analysis

The equipment for each model were sized and costed using the cost curve correlations in HysysPy, and the factorial method was used to determine the total capital investment (TCI) based on the equipment costs (Towler and Sinnott, 2022a). Custom units were defined for the air separation unit used to provide the O_2 feed for both models (Spallina et al., 2017) and the reforming reactor in the TRM route (Baliban et al., 2010; Graciano et al., 2018). The OCM reactors were costed as vessels, with their volume calculated using the catalyst mass and density, whilst assuming a 1 m/s superficial gas velocity through the bed (Penteado et al., 2018). Note that for simplification and extendability of the results, the capital cost for the electrification of the base process was not considered in this work. A 20 year lifetime for the plants and 10% interest rate were assumed to annualise the TCI, obtaining the Annualised Capital Charge (ACC).

For the raw material costs, CH_4 was assumed to bare no cost to the valorisation process, however, a cost for replacing the heating duty the CH_4 would have provided by renewable electricity was assumed. The required energy for this replacement was determined using the LHV of CH_4 and assuming that the original furnace where it was combusted had a 90% efficiency, whereas electrification would increase this efficiency to 100% (Son et al., 2022).

A nominal cost for the renewable electricity was based on the central estimate for onshore wind provided by BEIS (2023a), which equates to around 0.06 USD/kWh.

Note that since electricity consumption is the main driver for O_2 production in an air

separation unit, the cost of the O₂ feed was assumed to be a linear function based on the electricity intensity of the process. A value of 0.25 kWh/kg of O₂ was assumed in this work (Dowling and Biegler, 2015). Revenue is generated from the sale of the methanol and ethylene products from both routes, where an average price based on the historical market prices for both chemicals over 2018-2023 was used (Polymer Update, 2024). Fixed costs of production (FCP) were calculated according to the methodology by Towler and Sinnott (2022a).

Combining the ACC with the VCP, FCP and revenues from chemical sales, the levelised cost of CH₄ substitution (LCMS) was determined for each route:

$$\text{LCMS} = \frac{\text{ACC} + \text{VCP} + \text{FCP} - \text{REV}}{F_{\text{CH}_4}} \quad (6.4)$$

Where F_{CH_4} is the total CH₄ flowrate feed per year.

Comparison

The LCMS of both routes was compared to a business-as-usual (BAU) case, where the original process does not undergo electrification, and instead continues to combust the CH₄ side stream and pays a carbon tax on the resulting CO₂ emissions. With a nominal carbon tax value of 130 USD/tonne (Intergovernmental Panel On Climate Change, 2023b) combined with 2.75 kg of CO₂ emitted per kg of CH₄, this equates to a baseline cost of 0.36 USD/kg of CH₄.

Economic Feasibility

Expanding upon the techno-economic analysis based on nominal prices, the overall economic feasibility of both OCM and TRM was explored under varying market conditions at each CH₄ flowrate. The renewable electricity price, carbon tax (which effects both the BAU baseline and as well as the price of the direct emissions of both OCM and TRM) were varied. Additionally, a product premium (PP) on the methanol and ethylene products (PP) was investigated, varying from 1-2 times the market price. This metric is akin to the green premium metric used in Chapter 5.

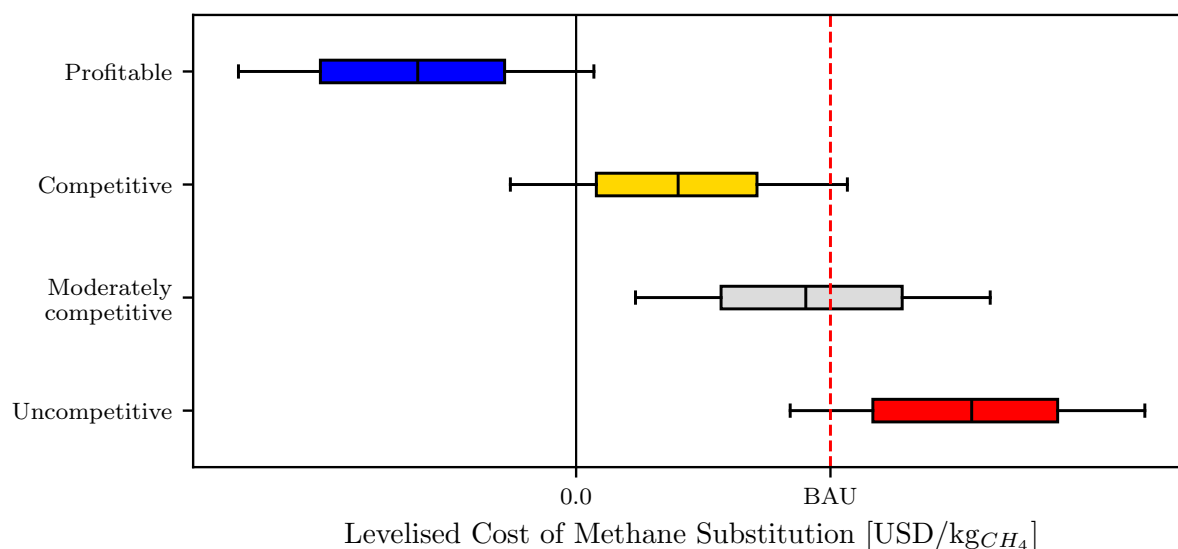


Figure 6.4: Visualisation of economic feasibility rankings based on levelised cost of processing distributions.

For each route, CH₄ scale, and PP, 768 samples for carbon tax and renewable electricity price pairs were generated using a Sobol sampling sequence (Herman and Usher, 2017).

Based on the 313 weekly market prices for methanol and ethylene over the 2018-2023 period, and assuming a triangular distribution for the CAPEX calculation between +/- 50% with five discrete bins, the cartesian product was used to create 1585 different market scenarios to be evaluated at each of the electricity and carbon tax samples. The LCMS for the routes were evaluated for each market scenario and the resulting LCMS distribution at that CH₄ feed scale, PP, electricity price, and carbon tax was compared to the BAU level. Based on the comparison of the LCMS distribution to the BAU cost, the following categorisation rules were used to indicate the performance of the route at those conditions:

- If 95% of LCMS values were less than zero, then that point was deemed **Profitable**.
- If 95% of LCMS values were less than the BAU price, then that point was categorised as **Competitive**.
- If $\geq 50\%$ of LCMS values were less than the BAU price, then that point was categorised as **Moderately Competitive**.

- If $< 50\%$ of LCMS values were less than the BAU price, then that point was categorised as **Uncompetitive**.

Figure 6.4 helps to illustrate this categorisation for each electricity price, carbon tax, PP and CH_4 flowrate. This categorisation combined with the exploration of many potential combinations of prices allows an understanding of the economic feasibility for both TRM and OCM.

Global Warming Potential

The global warming potential (GWP) was selected as the environmental KPI for comparing the performance of OCM and TRM. To obtain this, a life cycle assessment (LCA) was performed according to the ISO14040/14044 framework (ISO, 2006). First, goal and scope of the LCA was defined. The chosen functional unit was 1 kg of CH_4 feed and kWh of heating, based on the LHV of CH_4 (13.9 kWh/kg) and a 90% furnace efficiency. A zero-burden approach was used for the CH_4 feedstock i.e. no environmental impacts were associated with its production, which is a common assumption in LCAs for waste streams (Gentil et al., 2010). Additionally, a system expansion approach was used to account for the production of the methanol and ethylene products, where credits are received for avoiding their typical production routes. For methanol, this is natural gas reforming, and for ethylene, it is naphtha steam cracking.

HysysPy was used to extract the stream information from the HYSYS models to construct the life cycle inventories. The flowrates of each stream were normalised with respect to the CH_4 feed stream as the functional unit, along with the electricity and utilities. Note that as the base process has been electrified, it is also assumed that both the OCM and TRM routes have been electrified as well i.e. all heating and cooling utilities are driven by renewable electricity. The flows were then matched to corresponding inventories in the ecoinvent 3.10 database (Wernet et al., 2016) using Brightway2 as the LCA software (Mutel, 2017). For the impact assessment, the ReCiPe 2016 Midpoint method was used for the calculation (Huijbregts et al., 2017).

An uncertainty assessment was also performed using monte carlo sampling. Here,

1000 stochastically generated samples of the background processes were generated in Brightway2 using the pedigree matrices in the ecoinvent database (Weidema and Wesnæs, 1996).

6.3 Results and Discussion

6.3.1 Process Level Metrics

Table 6.1: Process level metrics for OCM and TRM routes.

Metric	Unit	OCM	TRM
Carbon efficiency	%	57.1	91.2
Product production rate	kg/kg _{CH₄}	0.50	1.95
Minimum heating requirement	kW/kg _{CH₄}	0	0
Minimum cooling requirement	kW/kg _{CH₄}	6.70	3.91
Electricity requirement	kW/kg _{CH₄}	0.80	0.94

Table 6.1 summarises the key process level metrics for both OCM and TRM across all the considered CH₄ feed flowrates. The first result is that the carbon efficiency of OCM is significantly lower than TRM, at 57% versus 91%, respectively. This is due to the CO₂ by-product formed in the OCM process, which is the thermodynamically favoured product at the reaction conditions of an OCM reactor. Therefore, even with recycling both ethane and re-converted CH₄ from H₂ and CO, and choosing a CH₄:O₂ ratio that maximises ethylene selectivity, the OCM catalyst is still not selective enough to achieve a higher ethylene yield. For the TRM route, the small carbon efficiency losses are due to unconverted CH₄ from the reforming process, which ends up being purged in the methanol synthesis section. However, the conversion of the TRM reactor at 950°C is already 97%, so there is little gain to be had by improving this conversion further. These differences in the carbon efficiency are reflected in the production capacity results for both process, with significantly more methanol being produced compared to ethylene.

For the utility requirements, both routes do not require any external heating, but have significant cooling requirements. As both of the main reactions are exothermic, there could exist potential for heat integration with the base plant depending on the

temperature requirements of the heating. OCM has a much larger cooling requirement compared to TRM, and the 6.70 kW/kg_{CH₄} of cooling equates to almost 430 MW of cooling at the largest 64 t/h CH₄ feed flowrate. This emphasises the strongly exothermic nature of the OCM reaction, and since it occurs at high temperature, there may be scope to use this heat to partially offset the CH₄ substitution costs, but utilising the reaction heat in place of CH₄ combustion. However, specific integration analysis is left as future work. Finally, the electricity requirements are very similar for both routes, with TRM requiring 18% more electricity due to the higher pressures required by its compression train.

6.3.2 CAPEX

Figure 6.5 shows the total capital investment of both OCM and TRM at the different CH₄ flowrates, as well as the percentage breakdown by equipment type. For the OCM route, at the lower CH₄ flowrates between 2 and 8 t/h, compressors are the greatest contribution to the TCI between 40-52%. However, as the CH₄ scale increases further, the heat exchange network (HEN) becomes the dominant capital cost factor, from 35% at 16t/h up to 47% at 64 t/h. This is due to the significant heat exchange duties, and subsequent required heat exchange area, required by the OCM route. A highly exothermic reaction section at high temperatures, coupled with poor per-pass conversions leading to high recycle rates, pushes the required heat exchange areas further. Additionally, heat exchangers do not benefit from economies of scale like other equipment; as their duty and area increase, the cost per m² actually increases. From the cost curve perspective, the scale exponent n is greater than 1, whereas for other equipment it is typically less than 1 (Towler and Sinnott, 2022a). As the HEN becomes the dominant contributing factor to the TCI, the economies of scale effect starts to reduce. This can be observed by comparing the increase in TCI from 16 to 32t/h to the subsequent increase up to 64t/h, where the TCI increases by a factor of 1.73 and 1.79, respectively.

For the TRM plant, the main cost contributor is the compressors from the compression train between the reforming and methanol synthesis reaction sections. This ranges from

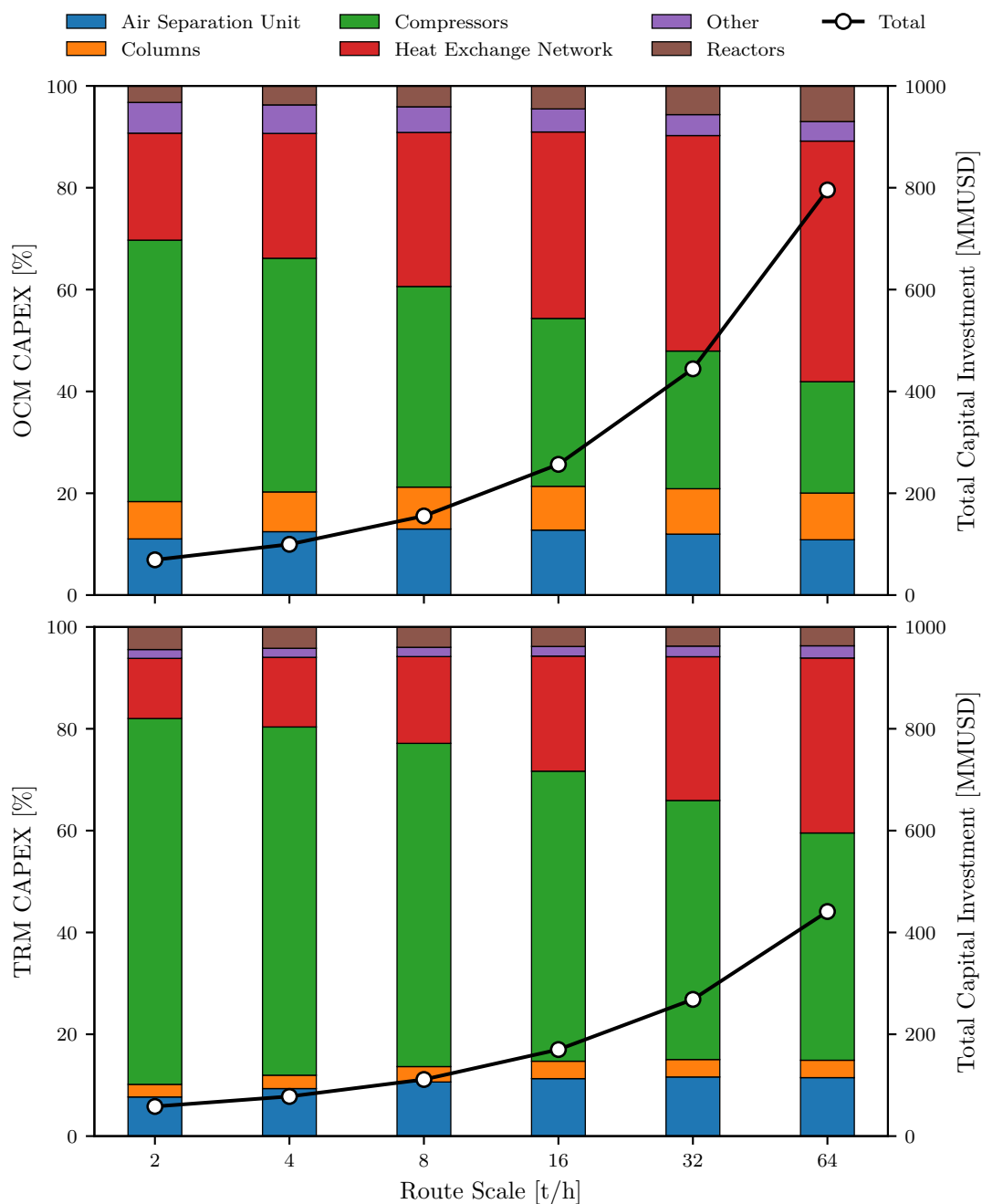


Figure 6.5: CAPEX breakdown and total capital investment for both OCM and TRM routes at different methane feed flowrates.

72% at 2t/h to 45% at 64 t/h. Whilst the HEN does take up an increasing proportion of the cost at higher scales, up to 34% in the 64t/h case, it is still low enough that economies of scale can continue to be realised up to the highest CH₄ flowrate considered in this work. For comparison with the OCM route, here the TCI increases from 268 MMUSD at 32 t/h to 441 MMUSD at 64 t/h, a 1.6 factor increase. In general, the other equipment costs across both routes contribute at most 29% of the capital costs, including the air separation unit for producing the pure O₂ feed.

Due to the aforementioned large heat exchange area, the OCM route requires a higher capital investment than the TRM route at every CH₄ flowrate. At 2t/h, the TCI for the OCM and TRM routes are 69 and 58 MMUSD, respectively, which corresponds to only a 17% increase in investment. However at 64t/h, this difference surges to an 80% increase, with the TRM route only requiring 441 MMUSD compared to the OCM route at 795 MMUSD. From a capital investment perspective, TRM is therefore significantly more attractive. For OCM to lower its required capital costs, the per-pass conversion must increase substantially whilst maintaining a similar ethylene selectivity. There is potential to optimise the OCM reaction layout further to achieve this (e.g. adjusting O₂ dosing ratios, feed temperatures, increasing number of reactors in series etc.), however this is left as future work.

A similar investigation was performed by Spallina et al. (2017), where a hypothetical OCM catalyst with 10x the reaction rate constant for reaction 6.2b was used in an OCM model. This realised a significant reduction in the capital costs of the process, with a 40% decrease compared to the current kinetic model. However, a factor of 10 increase in reaction rates is unlikely to be realised without any loss in other areas of catalyst performance.

For the TRM route, there is also scope to reduce the TCI further. As compressors constitute the main equipment costs, the operating pressure of the methanol synthesis section could be reduced from 78 bar. This will have a knock on effect on the cost of the reactor as per-pass conversions will reduce due to lower equilibrium conversion rates at lower pressures in methanol synthesis (Bussche and Froment, 1996).

6.3.3 Levelised Cost of CH₄ Substitution

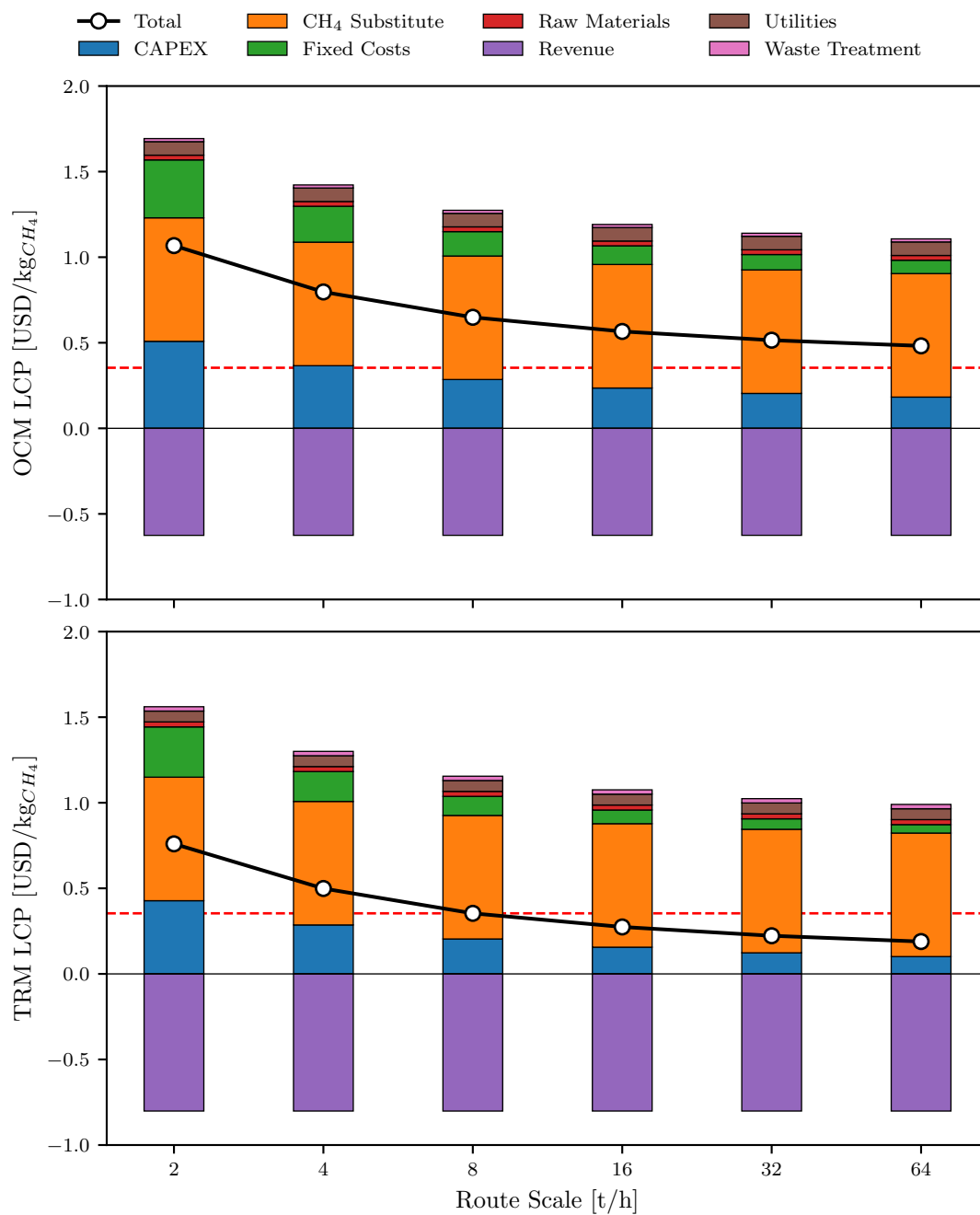


Figure 6.6: Breakdown of levelised cost of CH₄ substitution for both OCM and TRM at different CH₄ flowrates.

Figure 6.6 shows the breakdown of the LCMS for both OCM and TRM at the different CH₄ flowrates at the nominal price scenario. The BAU nominal cost is also shown for comparison, which at a carbon tax of 0.13 USD/kg, corresponds to an LCMS value of 0.36 USD/kg. At the average pricing scenario, both route are more expensive than the

BAU case at low CH₄ flowrates, at 1.06 USD/kg for OCM and 0.76 USD/kg for TRM at 2t/h. As the scale increases, both routes begin to benefit from economies of scale, as the capital costs per kg of CH₄ feed decrease, along with the fixed costs which are partially a function of the overall TCI.

For the OCM route, the LCMS decreases up to the maximum 64t/h flowrate, where it achieves an average LCMS of 0.48 USD/kg. Since the TCI is annualised in the LCMS calculations, the reduced economies of scale at the higher CH₄ becomes more apparent, with only a 6% decrease in LCMS from 32 to 64 t/h. This results in the average LCMS for OCM being uncompetitive with the BAU case across all CH₄ flowrates; the closest scale is at the maximum 64t/h where the LCMS is still 33% greater than the BAU case.

For the TRM route, the average LCMS decreases to 0.35 USD/kg at 8t/h, where the route becomes competitive with the BAU case. The LCMS continues decreasing until reaching its minimum value of 0.19 USD/kg at 64 t/h. At the scales presented in this work, the LCMS only decreases by 14% from 32t/h to 64t/h, so it is likely that there will be little benefit in increasing the scale further beyond this point. Whilst the TRM route does become competitive with the BAU case, it does not achieve overall profitability i.e. an LCMS less than or equal to zero. This means that whilst costs are lower than not undergoing fuel-switching via electrification and paying a carbon tax, if a carbon tax was not implemented, there would be no economic incentive to invest in either route as CH₄ valorisation processes.

Comparing the two routes directly, the revenues for the TRM route are greater than those of OCM, at 0.80 USD/kg versus 0.63 USD/kg respectively, or an 27% increase. Despite ethylene being a significantly more valuable chemical product than methanol (1.00 versus 0.34 USD/kg, respectively), the low carbon efficiency of the OCM route hinders its revenue generation potential and profitability.

In general for both routes, the greatest cost contributor across all scales is the CH₄ substitution costs with renewable electricity, which equals 0.72 USD/kg alone. It is clear therefore that the overall viability of these routes will be strongly linked to the price of renewable electricity, and is investigated further in Section 6.3.4. Capital costs are also

significant portion of the LCMS, especially at the lower CH_4 flowrates, at 0.50 USD/kg for OCM and 0.43 USD/kg at 2 t/h. Since the CH_4 substitution costs are identical across both routes, OCM has to i) reduce its TCI and/or ii) improve its carbon efficiency, if it is to become competitive with both the BAU case and TRM.

6.3.4 Economic Feasibility

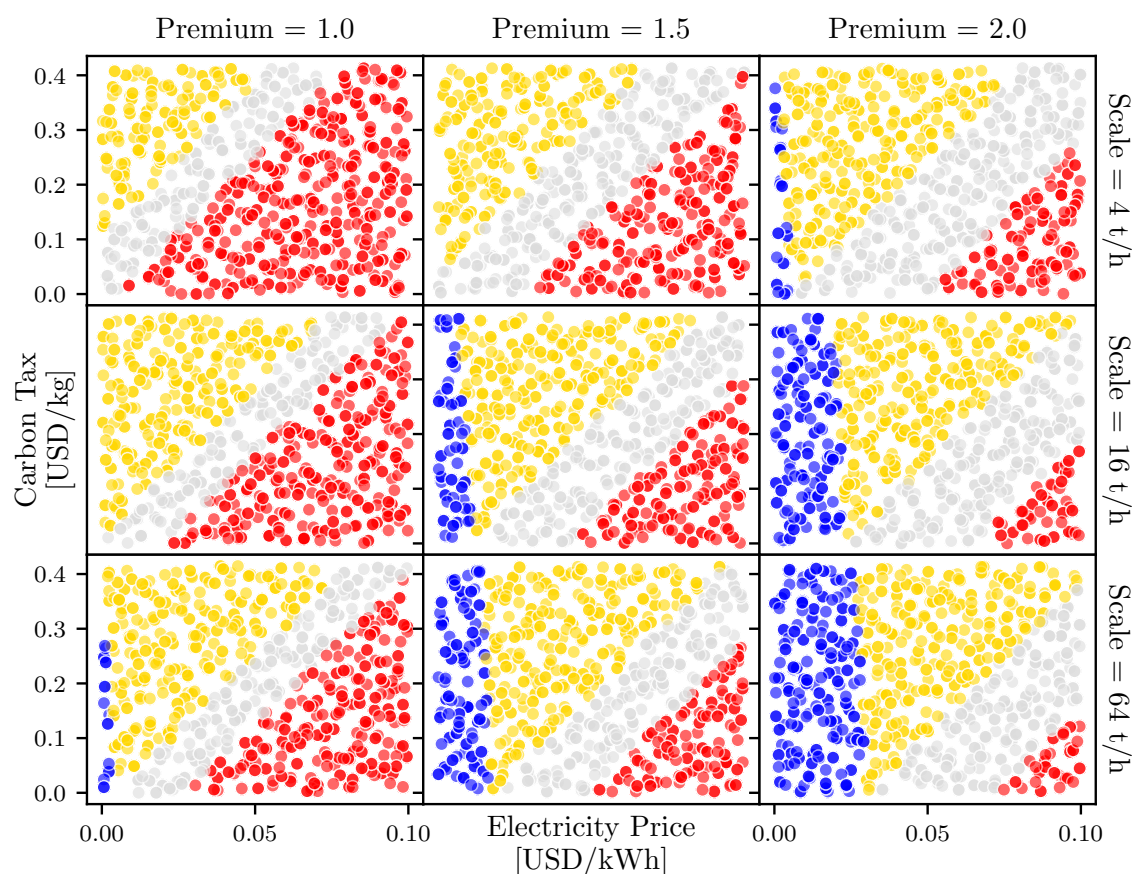


Figure 6.7: Economic feasibility plot for OCM route. Blue = profitable, yellow = competitive, grey = moderately competitive, red = uncompetitive.

Expanding on the LCMS results, Figure 6.7 shows a trellis plot of the OCM route at different scales, product premiums, carbon taxes and electricity prices. Note that for simplicity, only three of the CH_4 feed flowrates are shown for the rows of the trellis plot. Focusing first on the product premium of 1 column i.e. continuing to sell the ethylene at market price, it can be observed that the OCM route is uncompetitive for

a large portion of scenarios, especially at lower CH_4 flowrates, with 59% of economic design space points uncompetitive at 4t/h. There is a region of on the top left corner of the economic design space, where high carbon taxes hinder the BAU comparison, and the low renewable electricity prices reduce the cost of electrification, which were a significant portion of the LCMS as seen in Figure 6.6. As the scale increases down the column of the trellis plot, the region of competitiveness increases, as the CAPEX and fixed costs become a smaller contributor to the LCMS, and therefore OCM becomes competitive at lower carbon tax values and higher electricity prices. At the extreme corners of the competitive region for 4 t/h, the OCM route would need a 0.41 USD/kg carbon tax coupled with an 0.053 USD/kWh electricity rate, or free electricity and a carbon tax of 0.12 USD/kg. At the 64t/h scale, these bounds increase to the same 0.41 USD/kg carbon tax coupled with 0.072 USD/kWh of electricity, and wouldn't require any carbon tax to be competitive if the electricity source was free. Overall, increasing the scale of the process has improved the size of the competitive region from 21% to 40% of the economic feasibility space. The boundaries between the competitive and uncompetitive regions in Figure 6.7 exhibit a linear clustering pattern across the carbon tax and electricity price axes. This linearity reflects the direct mathematical relationship between the levelised cost of methane substitution and these two economic variables, wherein both carbon tax and electricity price contribute linearly to the overall process economics. Further illustrating the benefit of economies of scale, there are a small sample of profitable scenarios present at 64 t/h with approximately free renewable electricity. Whilst electricity prices are unlikely to ever be zero in the long term, there could be instances of very cheap electricity when renewable generation exceeds demand, and the electricity must be curtailed (Al-Ghussain et al., 2022).

As the product premium increases from 1 to 1.5 and 2, the region of competitiveness increases in size for all CH_4 flowrates, up to 40% for the 4 t/h scale. At a 1.5 PP, a small region of profitability also appears at very cheap electricity prices i.e. less than 0.012 USD/kWh for 16 and 64 t/h at PP of 1.5, and less than 0.023 USD/kWh at a PP of 2. Note that since carbon tax has only a very minor effect on the LCMS of the OCM route,

the carbon tax value has a negligible effect on the profitability region. Also note that the nominal price of renewable electricity of 0.06 USD/kWh is still substantially higher than that required for these regions of profitability. If the electricity price cannot fall to these levels, the OCM route will have to sell its ethylene product at ratios greater than 2 times market price to be profitable overall. This level of required product premium to break even is approaching that of CCU routes as was seen in the Flue2Chem case study in Chapter 5, where even free electricity and therefore H_2 prices still required a premium greater than 2. Whilst profitability will require large product premiums, competitiveness with the BAU case can be achieved at high levels of carbon tax. This emphasises the importance of policy drivers to incentivise net zero action.

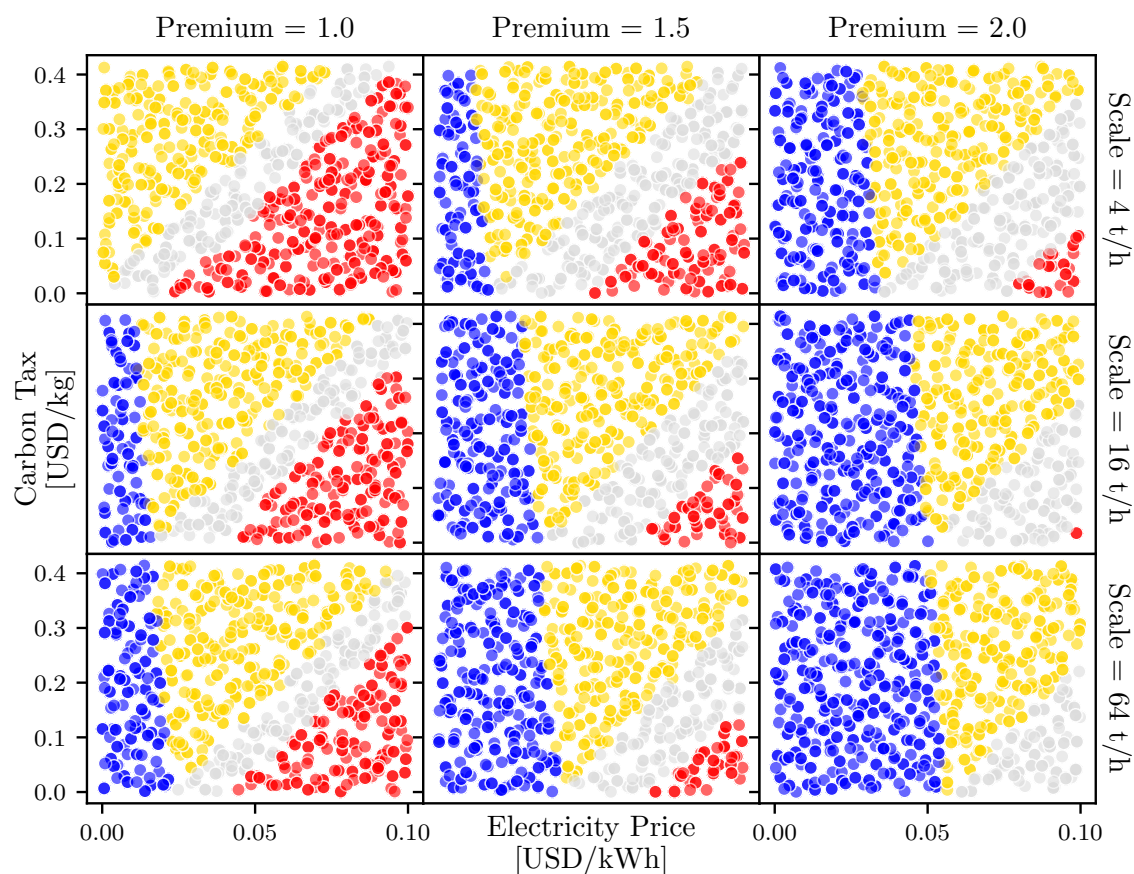


Figure 6.8: Economic feasibility plot for TRM route. Blue = profitable, yellow = competitive, grey = moderately competitive, red = uncompetitive.

By comparison, the economic feasibility plot of the TRM route is displayed in Figure

6.8. The regions of both competitiveness and profitability are much greater than was observed for OCM, with profitability achievable even at PP levels of 1 for both the 16 and 64 t/h cases, with 13–20% of sampled economic feasibility points achieving profitability. This corroborates the nominal LCMS results illustrated in Figure 6.6 that TRM has a lower LCMS across all CH₄ feedrates. Even though this profitability region still requires electricity prices to be less than or equal to 0.023 USD/kWh, this is still a substantial improvement over the OCM route. Expanding further, the competitive region is also greater in size: focusing on the 4t/h case at a PP of 1, the extreme bounds have now shifted to 0.067 USD/kWh at the maximum carbon tax, and at free electricity, carbon taxes can be as low as 0.01 USD/kg. Even at the average pricing scenario of 0.06 USD/kwh and 0.13 USD/kg for the carbon tax, the 16t/h and greater scales achieve competitiveness with the BAU case in over 95% of market scenarios. As observed with the OCM route, increasing the PP significantly increases the likelihood of both profitability and competitiveness with the BAU case, the most prominent of which is at the maximum 64 t/h scale and a premium of 2, where over 50% of sampled points are deemed profitable. In general, it can be concluded that the TRM route is much more likely to be profitable and competitive than the OCM route based on these results. A similar linear clustering of solution boundaries is observed in Figure 6.8, reflecting the same linear dependency on carbon tax and electricity price.

6.3.5 Global Warming Potential

Figure 6.9 displays the GWP results for the OCM and TRM routes, with both the nominal breakdown and distribution of GWP results obtained from the monte carlo analysis. The life cycle inventories are presented in Section D. Note that since the inventories are normalised per kg of CH₄ feed, all feed flowrate scales have the same inventory. TRM has the lower GWP at $-1.47\text{kg}_{\text{CO}_2e}$ with the OCM route at $-0.68\text{ kg}_{\text{CO}_2e}$ on average. Taking into account the background uncertainty in the ecoinvent database, the TRM results range from -2.03 to $-0.71\text{ kg}_{\text{CO}_2e}$, and OCM ranges from -1.20 to $0.03\text{ kg}_{\text{CO}_2e}$.

The first takeaway from these results is the substantial size of the credits received

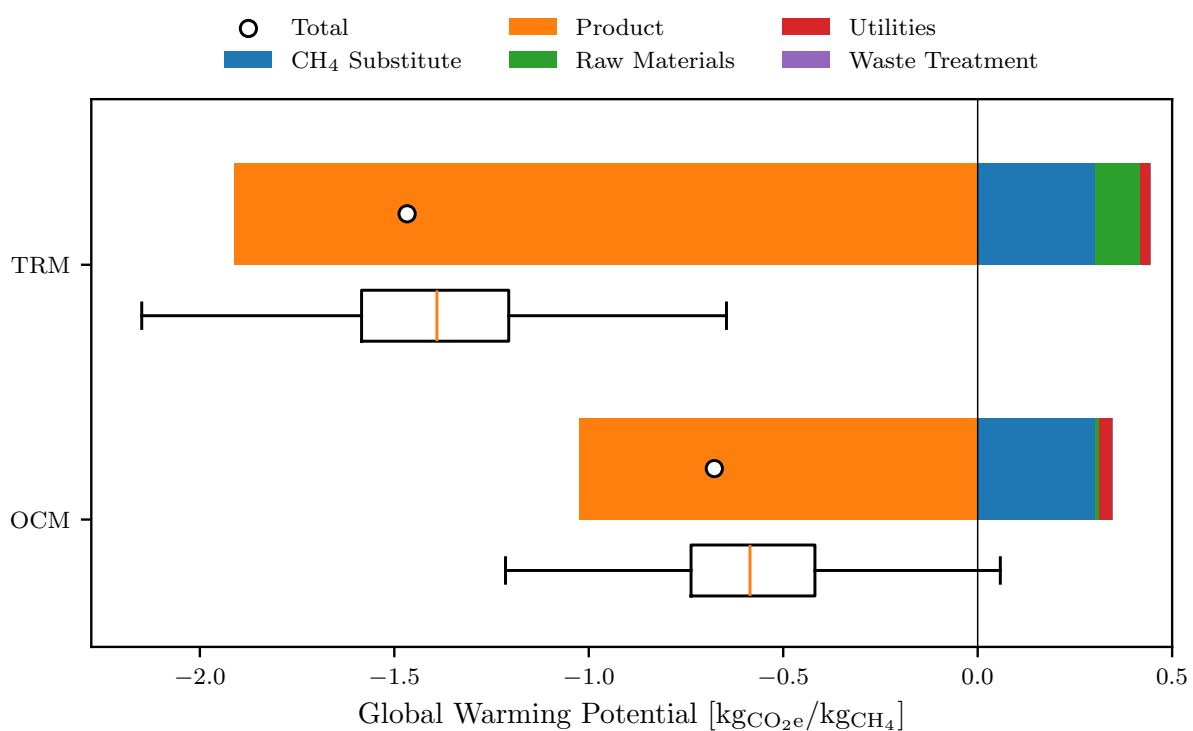


Figure 6.9: Global warming potential for OCM and TRM routes. Bars represent median values; offset box plots show the distribution resulting from Monte Carlo sampling of background life cycle inventory data, representing parameter uncertainty rather than measurement error.

for offsetting typical fossil fuel production routes, with 1.91 kg_{CO_{2e}} of credits for TRM and 1.02 kg_{CO_{2e}} credits for OCM. Since the typical routes for manufacturing methanol and ethanol are both energy and carbon intensive, substituting their manufacture with a greener alternative that uses renewable electricity as the primary energy source offers substantial environmental benefits. The process emissions i.e. the positive bars, are substantially lower than the offset credits, further reinforcing the benefit of avoiding typical fossil production routes. A caveat with these results is that not all CH₄ sources would be created equal from an environmental viewpoint. The results from CH₄ originating from biogenic sources e.g. anaerobic digestion of food waste, could potentially benefit from sequestration credits for storing the biogenic carbon within the chemical product, however, care must be taken when defining the system boundaries for an LCA that considers this.

Focusing on the positive process impacts, the electricity substitution is the largest contributor, at 0.30 kg_{CO_{2e}}. Even though a renewable source is being used, a substantial amount is required to replace 1 kg of CH₄ for heating purposes, which totals 12.5 kWh, as observed in Table D.1. The emissions due to construction of the renewable energy source (in this case wind turbines) still contribute a substantial amount to the life cycle of the renewable electricity generation. Comparing the two routes, the raw material contribution is substantially larger for TRM than OCM at 0.12 kg_{CO_{2e}} versus 0.01 kg_{CO_{2e}}, respectively. This is primarily due to the additional CO₂ feed required for the TRM route, which is considered to be an average of captured CO₂ using an amine-based capture process (MEA) from various different chemical processes as defined in ecoinvent 3.10.

For reference, assuming complete combustion, the BAU case would emit 2.75 kg_{CO_{2e}} per kg CH₄, significantly greater than the GWP for both these routes, even without considering system expansion credits. Furthermore, even if CCS was applied to the BAU case, a capture rate of 80–85% would be required to bring the GWP close to that of the positive process contributions from both OCM and TRM, which lie at 0.34 and 0.44 kg_{CO_{2e}}, respectively. This corroborates the results from Chapter 4, which illustrated the environmental benefit of coupling waste management with chemical manufacture. In essence, the same takeaway can be applied here, with the CH₄ feedstream treated as an

undesireable side product.

6.4 Conclusions

In conclusion, an enviro-economic assessment was performed to assess the feasibility of converting undesired CH_4 side streams into valuable chemicals. Assuming a base plant that previously used a by-product CH_4 stream as a fuel source decides to electrify their process, the viability of using either i) methanol production via tri-reforming of CH_4 or ii) ethylene production via oxidative coupling of CH_4 , was assessed. The routes were modelled with CH_4 feedrates ranging from 2t/h to 64t/h in Aspen HYSYS, with the enviro-economic assessment performed with the aid of HysysPy. A business-as-usual case is made assuming that the CH_4 continues to be combusted to close the energy balance for the base plant, and a carbon tax is paid on the resulting CO_2 emissions.

The TRM route possesses a much higher carbon efficiency at 91% compared to that of OCM at 57%, which suffers from high carbon losses to CO_2 as its reaction by-product. Additionally, the low per-pass conversion and high heating requirements lead to substantial heat exchange network and capital costs for OCM, reaching 795 MMUSD for the 64t/h feed flowrate case. Analysis on the overall economic feasibility of the OCM route reveals that it can be competitive with the BAU case under high carbon tax regimes and electricity prices lower than 0.053 USD/kWh. However, for the route to become profitable overall and not just cheaper than the BAU would require essentially free electricity, and selling the ethylene product at a minimum of 1.5 times market price. The TRM route, by comparison, has higher revenues thanks to the higher carbon efficiency and lower capital costs, and in general shows greater economic feasibility with larger regions of competitiveness in the economic design space. However, it still requires a combination of either very low electricity prices or selling the methanol product at above market price to become profitable. In general, scales above 8–16t/h are preferable for implementing either of these routes as below this the capital costs are too great to realise profitability.

In terms of global warming potential, both routes realise significant reductions in

emissions due to system expansion credits for avoiding typical manufacturing routes for methanol and ethylene. Even if the BAU process considered adding carbon capture, it would not be able to compete with the overall system benefits of renewable electricity based TRM and OCM routes considered in this work.

The main shortcoming of this work is the outdated kinetic model used for the OCM route. A microkinetic model, such as proposed by (Pirro et al., 2021), could also be implemented, and can be more easily implemented through the Python interface as illustrated in this work, instead of learning an additional modelling language for custom reactor operations e.g. ACM for Aspen HYSYS. In general, both routes could also benefit from optimisation to reduce their costs, especially OCM where operation and design of the reaction section will have significant impacts on the economic performance. Finally, a realistic case study should be performed where retrofit and integration opportunities are assessed and identified with the base plant undergoing electrification. In conclusion, this chapter confirms the GWP reductions from manufacturing chemicals from CH₄ side streams, and the required economic conditions to achieve both competitiveness and profitability.

Chapter 7

Conclusions

This thesis explores potential chemical pathways that shift ethylene production from a linear economy model towards a circular economy model. Through systematic investigation of under-researched circular feedstocks, development of unified assessment tools, and detailed process modelling, this research has provided new insights into viable pathways toward a more sustainable chemical industry.

7.1 Summary

In Chapter 3, HysysPy was introduced, a Python package that connects directly with Aspen HYSYS flowsheets to perform streamlined enviro-economic assessments. By maintaining a continuous connection from the process simulation through to both techno-economic analysis and life cycle assessment, HysysPy eliminates the manual data transfer workflows required by conventional disaggregated tools. Its capabilities were demonstrated through a case study investigating bioethylene production via ethanol dehydration from wheat fermentation. The bioethylene route was found to be economically competitive with steam cracking, especially in periods with low ethanol prices, and achieved reductions in cradle-to-gate GWP emissions. However, the assessment revealed significant burden shifting, with greater endpoint impacts to human health and ecosystem quality arising from the agricultural supply chain. This highlighted the caution that must be taken when assuming an “green” route that uses biomass as a feedstock is auto-

matically more sustainable overall. HysysPy then formed the methodological foundation for the subsequent assessments in this thesis, which explored various routes that enable circular ethylene production.

In Chapter 4, municipal solid waste gasification coupled with three different chemical manufacturing routes was assessed. The routes were methanol synthesis, ethanol synthesis via DME hydrocarbonylation, and olefins production via the methanol-to-olefins route. The analysis revealed that separating the CO₂ from the gasifier and sending it to storage in a CCS configuration led to economic competitiveness with incineration, as it reduced the required capital investment and the green H₂ demand. However, recycling the CO₂ in a carbon capture and utilisation (CCU) configuration was hampered by substantially higher green H₂ costs. Environmentally, the methanol and olefins routes offered significant reductions in impacts compared to both landfilling and incineration, primarily due to avoiding fossil-fuel based manufacturing of these chemicals. The ethanol route lacked these same benefits for the global warming potential, as it displaced bio-based ethanol production which already has favourable environmental performance. Nevertheless, all gasification routes demonstrated lower total enviro-economic costs than conventional waste management approaches, highlighting the potential benefit of coupling waste management solutions with chemical manufacture.

In Chapter 5, a novel process for a direct CO₂-to-ethanol catalyst was designed and its techno-economic performance assessed within a larger ethylene value chain. This route targeted ethylene production through subsequent ethanol dehydration, offering an alternative to the conventional methanol-to-olefins pathway that produces a mixed olefins stream. Carbon and energy efficiency metrics were evaluated for different process configurations, i.e. with and without pre-reactors to convert the unwanted methane by-product via either reverse water-gas shift or tri-reforming of methane. Without a pre-reactor, the carbon efficiency remained below 30% due to high methane formation rates and subsequent purge requirements, rendering the process economically unviable. Adding a pre-reactor improved carbon efficiency to 89% and made the route competitive with the indirect ethanol production pathway via DME hydrocarbonylation. However,

even with these improvements, green premiums remained above 7 due to green H_2 prices, and the route could not achieve economic competitiveness with the methanol-mediated pathway even under low-cost green H_2 scenarios. To improve competitiveness, catalyst development targets were quantified by systematically adjusting product selectivities and determining their impact on the overall green premium, revealing that methane formation rates would need to decrease by 90–99% to become competitive with the methanol mediated pathway.

In Chapter 6, the valorisation of methane side streams via chemical manufacture in fuel-switched processes was investigated. Two routes were compared: ethylene production via oxidative coupling of methane (OCM) and methanol production via tri-reforming of methane (TRM). The OCM route struggled with low per-pass conversions and poor ethylene yields, leading to substantial heat exchange requirements and capital costs of almost 800 MMUSD at the largest scale investigated (64 t/h of methane). The TRM route proved less capital intensive with higher revenues due to superior carbon efficiency (91% versus 57% for OCM). Both routes benefited from economies of scale, but economic analysis revealed that neither was likely to be competitive with simply combusting the methane and paying the associated carbon tax at scales below 8 t/h. Above these scales, TRM demonstrated greater potential for profitability owing to its higher revenues and lower capital requirements, but still requires low renewable electricity prices. Environmentally, both routes achieved significant reductions in global warming potential compared to the business-as-usual combustion case, analogous to the findings in Chapter 4, by combining the conversion of a waste stream with avoided fossil-based chemical manufacture.

7.2 Key Contributions

The main contributions of this work can therefore be summarised as follows:

- **Unified Enviro-Economic Assessment Framework:** Developed HysysPy to integrate process simulation, techno-economic analysis, and life cycle assessment, enabling faster enviro-economic evaluation across multiple chemical production routes.

- **MSW gasification viability:** Demonstrated that coupling MSW gasification with methanol or olefins production achieves lower enviro-economic costs than landfilling and incineration when integrated with CCS.
- **CO₂-to-ethanol catalyst targets:** Quantified that direct CO₂-to-ethanol catalysts likely require a 90–99% reduction in methane selectivity over current performance levels if they are to become economically competitive.
- **Methane valorisation potential:** Established that converting methane side-streams in fuel-switched processes is only likely to be cost competitive with combustion at scales above 8-16 t/h, and when coupled with high carbon tax and low renewable electricity prices.

7.3 Future Directions

The following areas have been identified as potential future directions to build upon the work presented in this thesis:

Automatic Flowsheet Generation Thanks to the improved enviro-economic assessment process enabled by the HysysPy framework, the most probable bottleneck for assessing a new chemical process is developing the process model. In most simulation software, this is a very time consuming and manual process requiring a lot of research and development time. However, with the rise of AI and its applications across multiple domains, it has been proposed that it should be possible to automate the creation of flowsheets using these tools. Gao and Schweidtmann (2023) presented an overview on how reinforcement-learning and agentic frameworks could be used to automatically create process flowsheets. If this kind of methodology is able to become more robust and deployed, it could reduce the required workload for performing enviro-economic assessments further. It could even give non-practioners the capability for assessing their process without modelling or EEA experience. An example of this is catalyst development teams automatically predicting the economic and environmental performance of their new catalyst without having to hire

an external team to perform the analysis. Coupled with a similar methodology as shown in Chapter 5, this would enable a quicker feedback loop for development targets, from experimental data all the way to models and EEAs for the predicted scaled up route.

Superstructure-based EEA of an Ethylene Cluster with Multiple Waste Feed-

stocks Many pathways were assessed throughout this thesis that could form part of a circular ethylene cluster in the future, as shown in the route map Figure 2.5. However, the next research direction should consider all of these potential routes simultaneously, and investigate scenarios for completely circular ethylene production from multiple renewable feedstocks. This would likely require a superstructure-based approach, and would also likely require creating surrogate models of the evaluated processes so they can be embedded within the superstructure (Henao and Maravelias, 2011). The use of surrogates within the superstructure would also enable the optimisation of each underlying process, an aspect which is missing from the analysis in this thesis. An initial hypothesis is that since all feedstocks have routes to methanol, those would be prioritised to take advantage of large economies of scale for the downstream MTO process, or even ethanol dehydration through DME hydrocarbonylation.

Planetary Boundaries Integration Whilst the LCA results that are generated during EEAs can reveal if a novel circular production route is better relative to the BAU fossil based route, it cannot be used to conclude if the route is sustainable enough in absolute terms. This is where incorporating the planetary boundaries framework (Steffen et al., 2015) to the assessment methodology would be beneficial. This framework sets to define a safe operating space for humanities activities with respect to the Earth's systems. It attempts to provide threshold levels for each of the considered systems via defined control variables for each system e.g. CO₂ concentration for climate change. The limits are set such that bypassing them will cause abrupt environmental change. Care must be taken though in proposing the appropriate share of the safe operating space in many of these circular production paths, especially when waste management is coupled with chemical manufacture as it becomes difficult to define what constitutes the safe operating space

when two different sectors are being merged together for the analysis.

Chemical Recycling within the Waste Hierarchy Across the routes that were assessed in this thesis, and beyond in the wider literature, a common result is that most of these circular production routes are more expensive than current fossil-fuel based routes. While costs are likely to continue to fall for routes that receive continued development and research, solutions need to be implemented as quickly as possible to achieve the industry's sustainability goals. This emphasises the need to prioritise the higher levels of the waste hierarchy i.e. reduce and re-use, as they are much more cost-effective options. Even for recycling technologies, mechanical recycling should still be preferred over chemical recycling where possible, as the energy requirements and costs are lower. Whilst chemical recycling routes will still form an important part in the circular economy transition, effort should be made to focus on how chemical recycling can complement these other levels to reduce the economic burden that they may place on existing supply chains.

Chapter 8

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Appendix A

HysysPy

Below shows the definition of the `DehydrationReactor` class, which calculated the reactor volume based on catalyst information from Kagyrmanova et al. (2011):

```
from hysyspy import PFR
import math as m

class DehydrationReactor(PFR):
    def __init__(self, op):
        super().__init__(op) # initialise with HYSYS operation

        # ghsv from kagyrmanova2011
        ref_etoh_feed = 60e3 # tonnes per year
        ref_etoh_feed *= 1000 / 8000 # kg/h, assuming 8000 h/y
        cat_mass = 4197 # kg
        overall_ghsv = ref_etoh_feed / cat_mass # kg/h/kg

        # using 4 reactors (mohsenzadeh2017)
        etoh_feed = self._feed.MassFlowValue * 3600 # kg/h of PFR feed
        overall_cat_mass = etoh_feed / overall_ghsv # kg
```

```

    # determining catalyst density from kagyrmanova2011 data

    d = 30e-3

    l = 3

    n = 2642

    vol = n * m.pi / 4 * d**2 * l

    cat_density = cat_mass / vol # kg/m3, bulk density

    # volume spread across 4 PFRs

    self.volume = overall_cat_mass / (cat_density * 4)

@property
def _diameter(self):

    return (self.volume * 4 / (5 * m.pi)) ** (1 / 3)

@property
def _height(self):

    """Assume 5 times the diameter"""

    return self._diameter * 5

```

As the volume, diameter, and height have been defined, the underlying PFR cost correlations can be used to cost the dehydration reactor.

Appendix B

MSW Gasification

Stream Tables

The stream tables presented in this section refer to the nominal MSW feed case with CO₂ recycling (i.e. the CCU case).

MSW Processing and Gasification

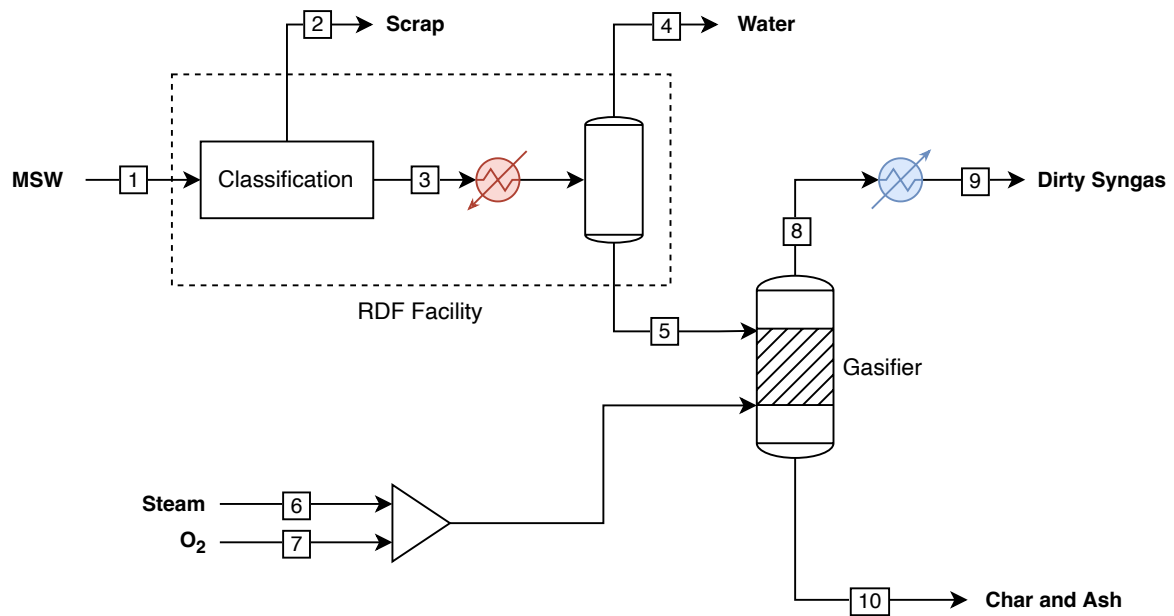


Figure B.1: Flow diagram for MSW processing and gasification section

Table B.1: Stream table for MSW processing and gasification

Stream Name	1	2	3	4	5	6	7	8	9	10
Temperature [°C]	25.0	25.0	25.0	25.0	25.0	25.0	25.0	750.0	35.0	750.0
Pressure [bar]	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Vapour Fraction	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	0.92	0.00
Mass Flow [t/h]	73.33	14.67	58.67	15.10	43.57	8.84	18.75	68.82	68.82	2.33
Composition [wt%]										
MSW*	65.35	65.35	65.35	0.00	88.00	0.00	0.00	0.00	0.00	0.00
Carbon	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	17.93
Ash*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	82.07
Methane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.39	0.39	0.00
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	49.16	49.16	0.00
CO2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	30.89	30.89	0.00
Hydrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.94	4.94	0.00
H2O	34.65	34.65	34.65	100.00	12.00	100.00	0.00	13.43	13.43	0.00
Oxygen	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00
Nitrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	0.00
Ammonia	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H2S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.20	0.20	0.00

Syngas Cleanup

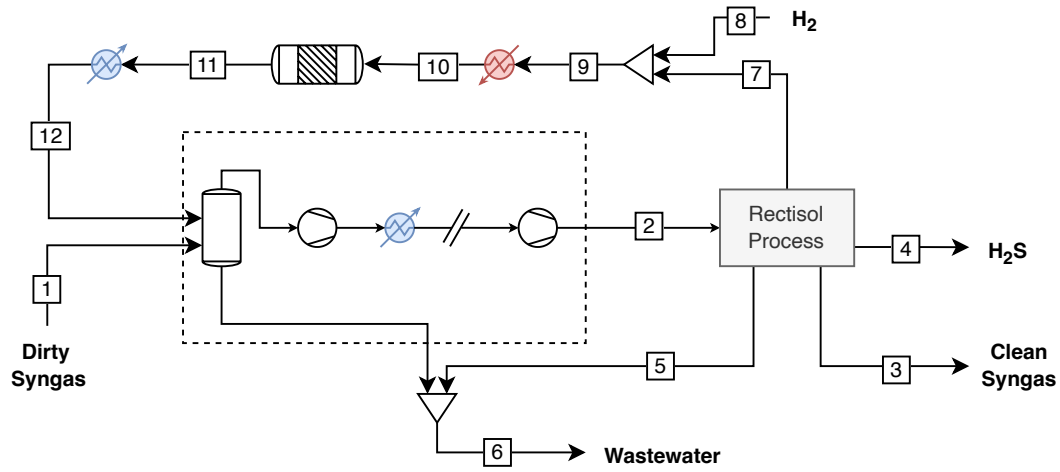


Figure B.2: Flow diagram for syngas cleanup section

Table B.2: Stream table for syngas cleanup section (1/2)

Stream Name	1	2	3	4	5	6
Temperature [°C]	35.0	180.3	-39.9	40.0	15.0	31.5
Pressure [bar]	1.00	26.25	26.25	3.20	26.25	1.00
Vapour Fraction	0.92	1.00	1.00	0.99	0.36	0.04
Mass Flow [t/h]	68.82	84.63	52.55	1.07	1.36	16.73
Composition [wt%]						
Methane	0.39	0.32	0.49	0.00	0.00	0.01
Carbon-Dioxide	30.89	40.96	8.62	79.29	0.00	2.33
Carbon-Monoxide	49.16	52.15	83.15	0.00	0.00	0.29
Hydrogen	4.94	4.80	7.72	0.00	0.00	0.00
Ammonia	0.00	0.00	0.00	0.00	0.04	0.00
Hydrogen-Sulfide	0.20	0.15	0.00	11.49	0.00	0.02
Water	13.43	0.80	0.00	0.00	49.61	93.21
Nitrogen	1.00	0.81	0.00	0.00	50.35	4.11

Table B.3: Stream table for syngas cleanup section (2/2)

Stream Name	7	8	9	10	11	12
Temperature [°C]	-42.2	25.0	-13.2	900.0	900.0	35.0
Pressure [bar]	3.00	30.00	3.00	3.00	3.00	3.00
Vapour Fraction	1.00	1.00	1.00	1.00	1.00	0.75
Mass Flow [t/h]	29.81	1.37	31.18	31.18	31.18	31.18
Composition [wt%]						
Methane	0.03	0.00	0.03	0.03	0.01	0.01
Carbon-Dioxide	98.42	0.00	94.10	94.10	44.23	44.23
Carbon-Monoxide	1.48	0.00	1.41	1.41	33.20	33.20
Hydrogen	0.03	100.00	4.41	4.41	2.14	2.14
Ammonia	0.00	0.00	0.00	0.00	0.00	0.00
Hydrogen-Sulfide	0.00	0.00	0.00	0.00	0.00	0.00
Water	0.00	0.00	0.00	0.00	20.39	20.39
Nitrogen	0.00	0.00	0.00	0.00	0.00	0.00

Rectisol Process

The following version of the Rectisol process is based on the model developed by Yang et al. (2016b).

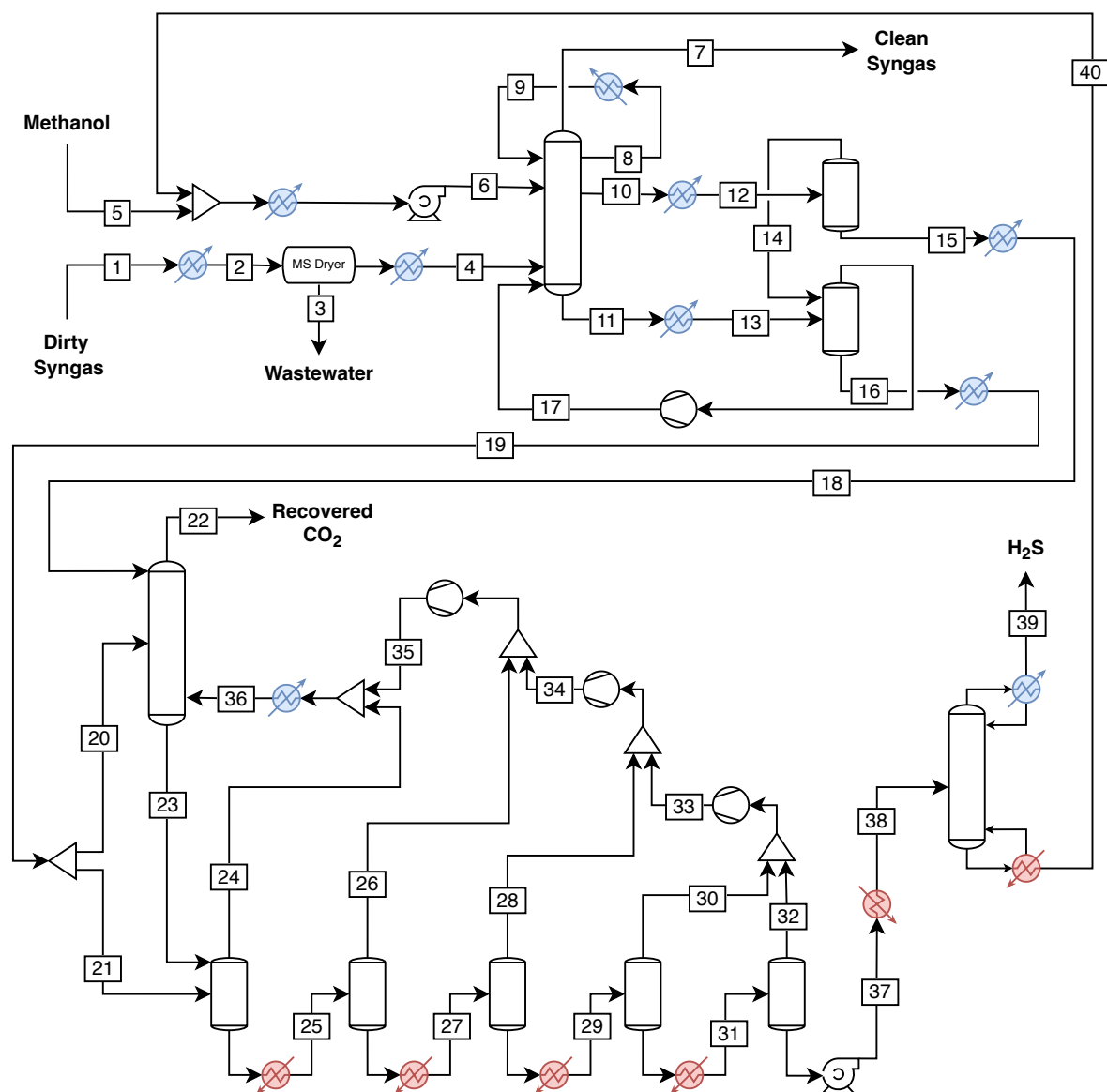


Figure B.3: Flow diagram for Rectisol process

Stream Name	1	2	3	4	5	6	7	8	9	10
Temperature [°C]	180.3	15.0	15.0	-21.0	96.7	-49.1	-39.9	-26.7	-40.0	-24.7
Pressure [bar]	26.25	26.25	26.25	26.25	3.20	26.50	26.25	26.25	26.25	26.25
Vapour Fraction	1.00	0.99	0.39	1.00	1.00	0.00	1.00	0.00	0.00	0.00
Mass Flow [t/h]	84.63	84.63	1.36	83.27	0.00	213.64	52.55	146.73	146.83	110.29
Composition [wt%]										
Methane	0.32	0.32	0.00	0.32	0.00	0.00	0.49	0.01	0.01	0.01
Carbon-Dioxide	40.96	40.96	0.00	41.63	0.00	0.00	8.62	12.05	12.03	12.83
Carbon-Monoxide	52.15	52.15	0.00	53.00	0.00	0.00	83.15	0.37	0.37	0.36
Methanol	0.01	0.01	0.00	0.01	100.00	99.99	0.02	87.55	87.57	86.78
Hydrogen	4.80	4.80	0.00	4.88	0.00	0.00	7.72	0.01	0.01	0.01
Hydrogen-Sulfide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	0.80	0.80	49.61	0.00	0.00	0.01	0.00	0.01	0.01	0.01
Nitrogen	0.81	0.81	50.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00

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[illegible]

Methanol Synthesis

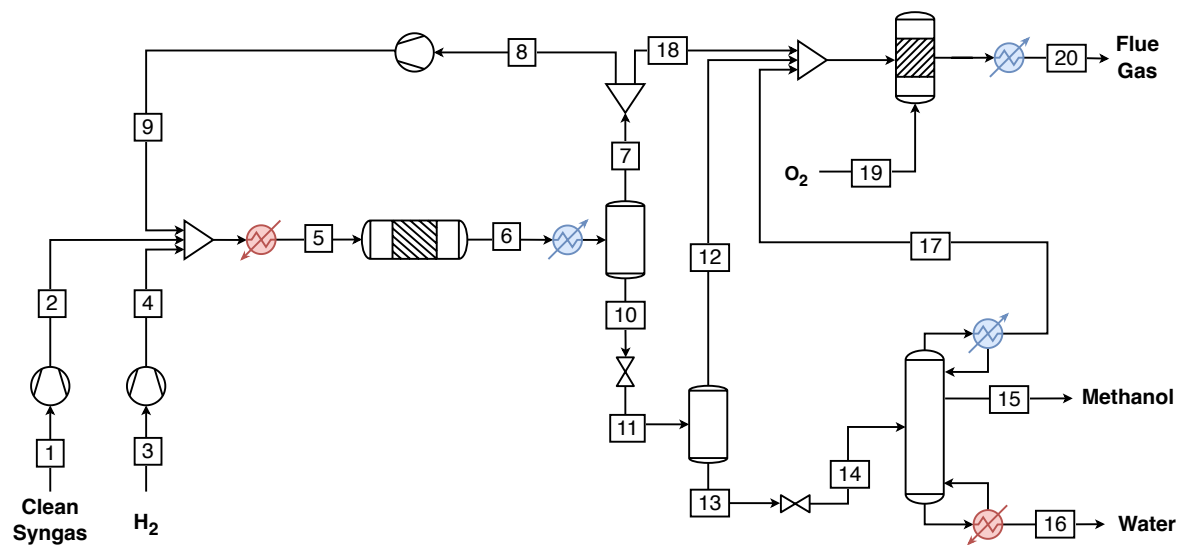


Figure B.4: Flow diagram for methanol synthesis section

Table B.8: Stream table for methanol synthesis (1/2)

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Methanol-to-Olefins

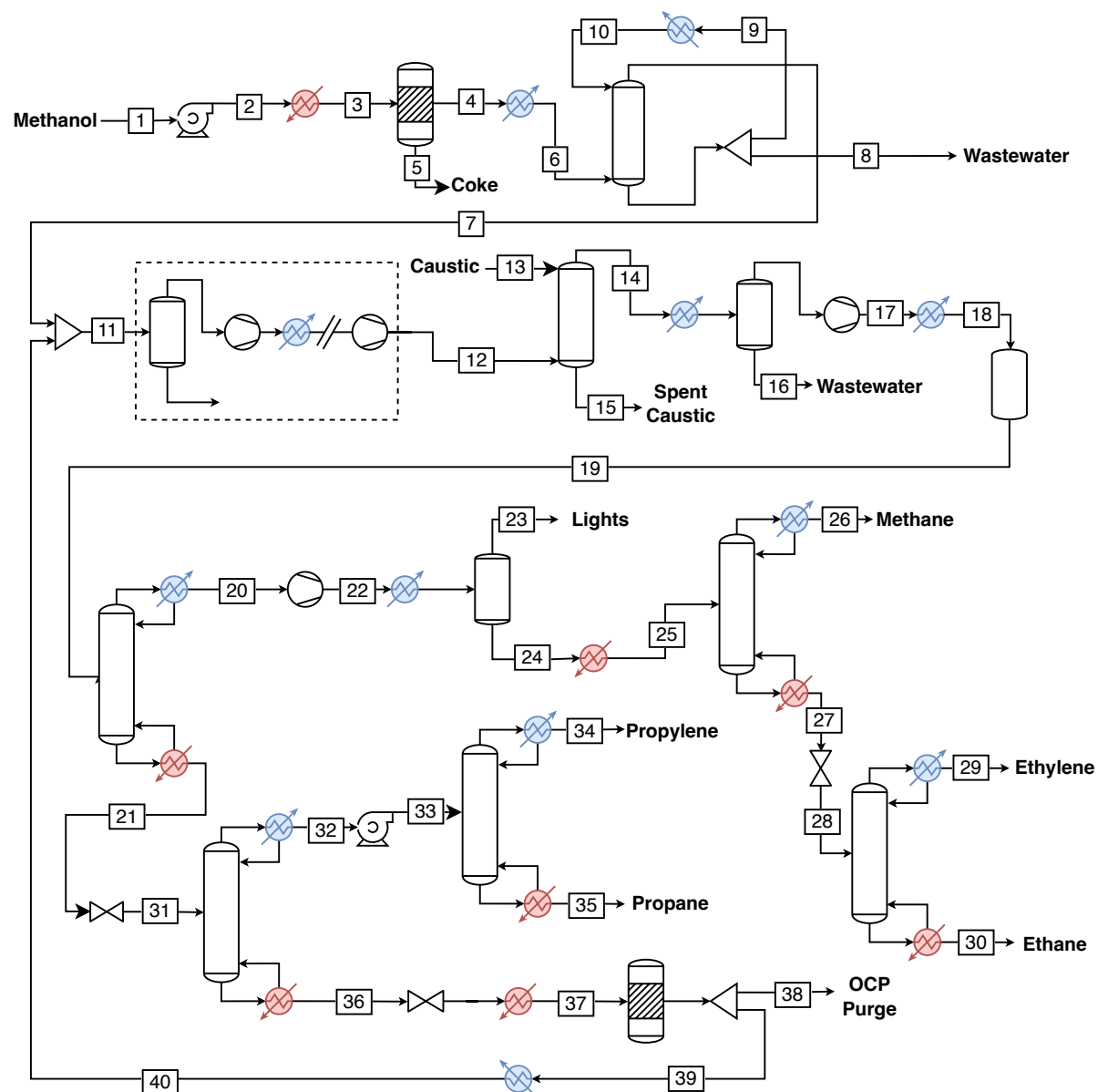


Figure B.5: Flow diagram for methanol-to-olefins section

Table B.10: Stream table for methanol-to-olefins (1/4)

Stream Name	1	2	3	4	5	6	7	8	9	10
Temperature [°C]	63.0	63.0	410.0	410.0	410.0	101.6	35.0	101.5	101.5	35.0
Pressure [bar]	1.00	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Vapour Fraction	0.00	0.00	1.00	1.00	0.00	1.00	1.00	0.00	0.00	0.00
Mass Flow [t/h]	48.87	48.87	48.87	48.22	0.65	48.22	21.16	24.99	224.91	224.91
Composition [wt%]										
Methane	0.00	0.00	0.00	1.06	0.00	1.06	2.41	0.00	0.00	0.00
Ethane	0.00	0.00	0.00	0.36	0.00	0.36	0.82	0.00	0.00	0.00
Propane	0.00	0.00	0.00	0.23	0.00	0.23	0.52	0.00	0.00	0.00
n-Butane	0.00	0.00	0.00	0.04	0.00	0.04	0.09	0.00	0.00	0.00
Ethylene	0.00	0.00	0.00	16.91	0.01	16.91	38.49	0.03	0.03	0.03
Propylene	0.00	0.00	0.00	16.91	0.03	16.91	38.51	0.01	0.01	0.01
1-Butene	0.00	0.00	0.00	5.21	0.02	5.21	11.88	0.00	0.00	0.00
1-Pentene	0.00	0.00	0.00	2.13	0.01	2.13	4.85	0.00	0.00	0.00
Hydrogen	0.00	0.00	0.00	0.07	0.00	0.07	0.15	0.00	0.00	0.00
Carbon-Monoxide	0.00	0.00	0.00	0.01	0.00	0.01	0.03	0.00	0.00	0.00
Carbon-Dioxide	0.03	0.03	0.03	0.08	0.00	0.08	0.18	0.00	0.00	0.00
Water	0.01	0.01	0.01	56.79	0.74	56.79	2.03	99.80	99.80	99.80
Methanol	99.97	99.97	99.97	0.20	0.01	0.20	0.03	0.15	0.15	0.15
Carbon-Graphite	0.00	0.00	0.00	0.00	99.19	0.00	0.00	0.00	0.00	0.00
NaOH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table B.11: Stream table for methanol-to-olefins (2/4)

Stream Name	11	12	13	14	15	16	17	18	19	20
Temperature [°C]	47.5	90.6	25.1	75.4	75.0	40.0	92.2	15.0	15.0	-39.7
Pressure [bar]	1.50	7.75	7.74	7.74	7.74	7.74	17.59	17.59	17.59	17.00
Vapour Fraction	1.00	1.00	0.00	1.00	0.00	0.00	1.00	0.62	0.63	1.00
Mass Flow [t/h]	26.06	25.92	0.93	26.07	0.78	0.53	25.55	25.55	25.41	9.39
Composition [wt%]										
Methane	1.98	2.00	0.00	1.98	0.00	0.00	2.02	2.02	2.04	5.51
Ethane	0.67	0.68	0.00	0.67	0.00	0.00	0.69	0.69	0.69	1.86
Propane	0.42	0.42	0.00	0.42	0.00	0.00	0.43	0.43	0.43	0.00
n-Butane	0.07	0.07	0.00	0.07	0.00	0.00	0.07	0.07	0.08	0.00
Ethylene	33.26	33.44	0.00	33.14	3.35	0.00	33.82	33.82	34.01	92.06
Propylene	42.42	42.64	0.00	42.14	8.43	0.00	43.00	43.00	43.24	0.16
1-Butene	13.92	13.99	0.00	13.72	6.33	0.00	14.01	14.01	14.08	0.00
1-Pentene	5.28	5.31	0.00	5.16	3.95	0.00	5.26	5.26	5.29	0.00
Hydrogen	0.12	0.12	0.00	0.12	0.00	0.00	0.12	0.12	0.12	0.34
Carbon-Monoxide	0.02	0.02	0.00	0.02	0.00	0.00	0.03	0.03	0.03	0.07
Carbon-Dioxide	0.15	0.15	0.00	0.00	4.91	0.00	0.00	0.00	0.00	0.00
Water	1.65	1.14	85.00	2.54	54.39	100.00	0.54	0.54	0.00	0.00
Methanol	0.02	0.02	0.00	0.00	0.76	0.00	0.00	0.00	0.00	0.00
Carbon-Graphite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NaOH	0.00	0.00	15.00	0.00	17.87	0.00	0.00	0.00	0.00	0.00

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Ethanol via DME Hydrocarbonylation

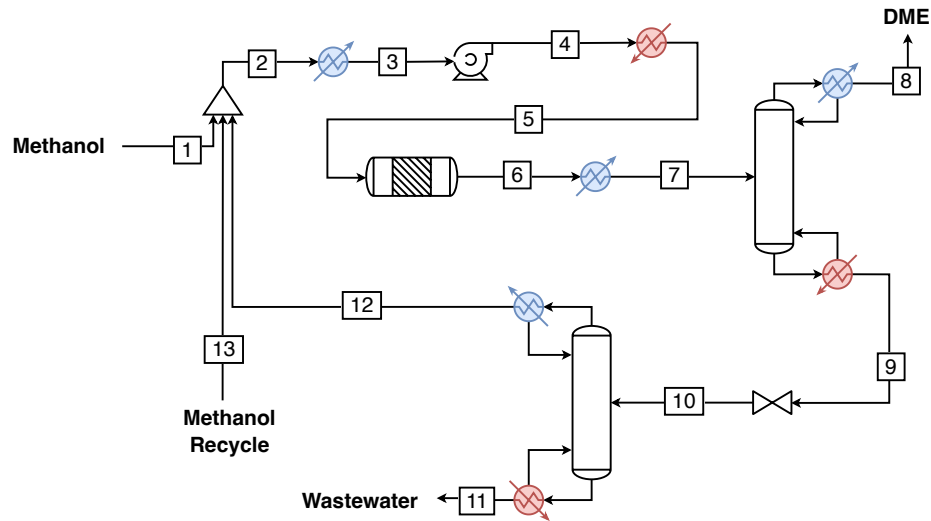


Figure B.6: Flow diagram for DME synthesis

Table B.14: Stream table for DME synthesis within ethanol synthesis (1/2)

Stream Name	1	2	3	4	5	6	7
Temperature [°C]	63.0	64.4	35.0	35.3	275.0	387.6	149.6
Pressure [bar]	1.00	1.00	1.00	12.00	12.00	11.50	11.50
Vapour Fraction	0.00	0.20	0.00	0.00	1.00	1.00	1.00
Mass Flow [t/h]	24.43	60.01	60.01	60.01	60.01	60.01	60.01
Composition [wt%]							
Methane	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Carbon-Dioxide	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Carbon-Monoxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Methanol	99.98	95.89	95.89	95.89	95.89	17.11	17.11
Hydrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	0.01	0.11	0.11	0.11	0.11	22.26	22.26
Dimethyl-Ether	0.00	0.08	0.08	0.08	0.08	56.72	56.72
Ethanol	0.00	3.70	3.70	3.70	3.70	3.70	3.70
Acetates	0.00	0.21	0.21	0.21	0.21	0.21	0.21

Table B.15: Stream table for DME synthesis within ethanol synthesis (2/2)

Stream Name	8	9	10	11	12	13
Temperature [°C]	44.4	149.9	88.5	66.4	105.2	64.2
Pressure [bar]	10.00	10.50	1.50	1.00	1.30	1.00
Vapour Fraction	0.00	0.00	0.07	1.00	0.00	0.00
Mass Flow [t/h]	34.01	25.99	25.99	12.45	13.54	23.30
Composition [wt%]						
Methane	0.00	0.00	0.00	0.00	0.00	0.00
Carbon-Dioxide	0.01	0.00	0.00	0.00	0.00	0.00
Carbon-Monoxide	0.00	0.00	0.00	0.00	0.00	0.00
Methanol	0.07	39.41	39.41	80.36	1.77	99.82
Hydrogen	0.00	0.00	0.00	0.00	0.00	0.00
Water	0.00	51.38	51.38	0.53	98.12	0.00
Dimethyl-Ether	99.91	0.20	0.20	0.41	0.00	0.00
Ethanol	0.00	8.53	8.53	17.69	0.11	0.17
Acetates	0.00	0.48	0.48	1.01	0.00	0.01

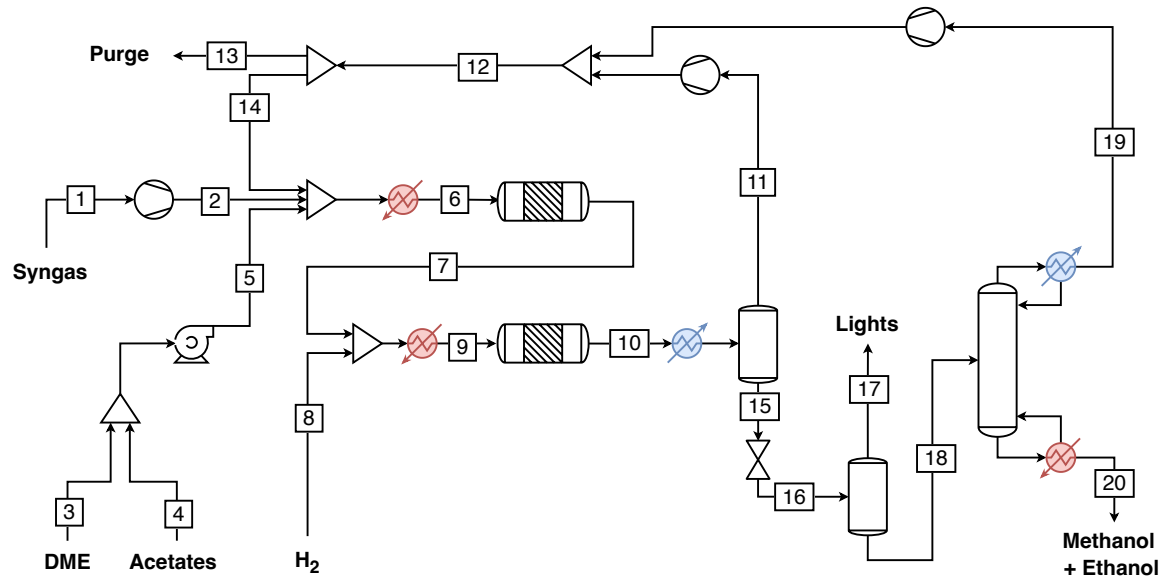


Figure B.7: Flow diagram for hydrocarbonylation of DME

Table B.16: Stream table for DME hydrocarbonylation section within ethanol synthesis (1/2)

Stream Name	1	2	3	4	5	6	7	8	9	10
Temperature [°C]	-39.9	-0.0	44.4	57.3	48.6	175.0	175.0	150.9	260.0	260.0
Pressure [bar]	26.25	40.00	10.00	10.00	40.00	40.00	39.50	78.00	39.50	39.00
Vapour Fraction	1.00	1.00	0.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00
Mass Flow [t/h]	26.28	26.28	34.01	4.99	39.00	248.90	248.90	0.98	249.88	249.88
Composition [wt%]										
Methane	0.49	0.49	0.00	0.00	0.00	2.29	2.29	0.00	2.29	2.29
Carbon-Dioxide	8.62	8.62	0.01	0.00	0.01	31.45	31.45	0.00	31.33	31.33
Carbon-Monoxide	83.15	83.15	0.00	0.00	0.00	39.31	31.13	0.00	31.01	31.01
Methanol	0.02	0.02	0.07	51.85	6.69	1.49	1.49	0.00	1.48	10.80
Hydrogen	7.72	7.72	0.00	0.00	0.00	2.56	2.56	100.00	2.94	1.77
Dimethyl-Ether	0.00	0.00	99.91	1.44	87.33	21.55	8.10	0.00	8.07	8.07
Ethanol	0.00	0.00	0.00	0.00	0.00	0.32	0.32	0.00	0.32	13.71
Methyl-Acetate	0.00	0.00	0.00	2.31	0.29	0.05	21.68	0.00	21.60	0.05
Ethyl-Acetate	0.00	0.00	0.00	44.40	5.68	0.97	0.97	0.00	0.97	0.97

Table B.17: Stream table for DME hydrocarbonylation section within ethanol synthesis (2/2)

Stream Name	11	12	13	14	15	16	17	18	19	20
Temperature [°C]	35.0	41.5	41.5	41.5	35.0	32.6	32.6	32.6	36.9	155.3
Pressure [bar]	39.00	40.00	40.00	40.00	39.00	15.00	15.00	15.00	14.50	15.00
Vapour Fraction	1.00	1.00	1.00	1.00	0.00	0.04	1.00	0.00	1.00	0.00
Mass Flow [t/h]	172.74	185.80	2.22	183.62	77.14	77.14	2.36	74.78	13.06	61.72
Composition [wt%]										
Methane	3.24	3.04	3.04	3.04	0.15	0.15	2.80	0.07	0.40	0.00
Carbon-Dioxide	41.54	41.39	41.40	41.40	8.47	8.47	58.39	6.90	39.49	0.00
Carbon-Monoxide	44.39	41.39	41.39	41.39	1.04	1.04	24.75	0.29	1.68	0.00
Methanol	0.63	0.59	0.59	0.59	33.57	33.57	0.94	34.60	0.07	41.91
Hydrogen	2.53	2.36	2.36	2.36	0.05	0.05	1.20	0.01	0.06	0.00
Dimethyl-Ether	7.07	10.67	10.67	10.67	10.30	10.30	11.10	10.28	58.29	0.12
Ethanol	0.46	0.43	0.43	0.43	43.38	43.38	0.65	44.73	0.01	54.20
Methyl-Acetate	0.01	0.01	0.01	0.01	0.15	0.15	0.02	0.15	0.00	0.19
Ethyl-Acetate	0.12	0.11	0.11	0.11	2.88	2.88	0.16	2.96	0.00	3.59

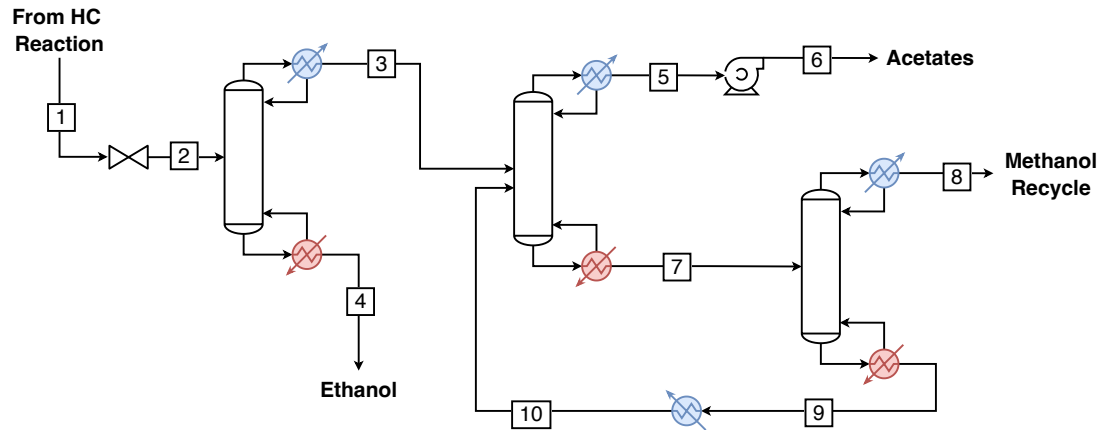


Figure B.8: Flow diagram of ethanol separation section

Table B.18: Stream table for separation section within ethanol synthesis

Stream Name	1	2	3	4	5	6	7	8	9	10
Temperature [°C]	155.3	79.7	60.1	88.6	56.2	57.3	67.7	64.2	256.4	40.0
Pressure [bar]	15.00	1.50	1.00	1.50	1.00	10.00	1.00	1.00	1.00	1.00
Vapour Fraction	0.00	0.28	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.00
Mass Flow [t/h]	61.72	61.72	28.28	33.43	4.99	4.99	30.99	23.30	7.70	7.70
Composition [wt%]										
Methane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbon-Dioxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbon-Monoxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Methanol	41.91	41.91	91.37	0.07	51.85	51.85	75.04	99.82	0.00	0.00
Hydrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dimethyl-Ether	0.12	0.12	0.25	0.00	1.44	1.44	0.00	0.00	0.00	0.00
Ethanol	54.20	54.20	0.14	99.93	0.00	0.00	0.12	0.17	0.00	0.00
Methyl-Acetate	0.19	0.19	0.41	0.00	2.31	2.31	0.00	0.00	0.00	0.00
Ethyl-Acetate	3.59	3.59	7.83	0.00	44.40	44.40	0.01	0.01	0.00	0.00
Glycerol	0.00	0.00	0.00	0.00	0.00	0.00	24.83	0.00	100.00	100.00

Waste Composition

Table B.19: Composition of various wastes fed to gasification routes (Bridgwater et al., 2019a)

Property	Unit	Amount		
		MSW	BIO	MPW
Waste Composition ¹				
Food waste	wt%	46.9	64.4	0
Garden waste	wt%	4.6	6.3	0
Paper	wt%	12.9	17.7	0
Card	wt%	5.3	7.3	0
Mixed plastic ²	wt%	19.2	0	98.4
Textiles	wt%	7.4	0	0
Wood	wt%	1.9	2.7	0
Fines	wt%	1.6	1.6	1.6
Ultimate Analysis (dry basis)				
Carbon	wt%	54.6	46.6	84.5
Hydrogen	wt%	7.7	6.2	13.5
Nitrogen	wt%	1.8	2.0	0.1
Sulphur	wt%	0.3	0.3	0.4
Oxygen	wt%	30.6	38.8	0.1
Ash	wt%	5.0	6.1	1.4
HHV (dry basis) ³	MJ/kg	24.9	19.5	45.4
Moisture (wet basis) ⁴	wt%	34.7	34.7	34.7

¹ Used ultimate analysis estimation from Tchobanoglous et al. (1993) for each waste subgroup to determine the overall ultimate analysis presented below.

² Mixture of PE, PP and PS as defined in Salah et al. (2023b).

³ Estimated using the correlation defined by Channiwala and Parikh (2002).

⁴ Moisture value taken from typical UK MSW composition (Cross et al., 2021b).

Equipment CAPEX Correlations

The cost correlations used for standard equipment (i.e. pumps, vessels, compressors etc.) are from Towler and Sinnott (2022b). The specialised equipment shown below in Table B.20 use the following correlation to determine the purchased equipment cost:

$$C = C_0 \left(\frac{S}{S_0} \right)^n \quad (\text{B.1})$$

Table B.20: Equipment cost curves for specialised equipment. All correlations below use 2014 as the reference year.

Equipment	C₀ [MUSD]	S₀	S Variable	n	Reference
RDF Facility	94.82	45.2	MSW feed (kg/s)	0.77	Niziolek et al. (2015b)
Gasifier	54.11	17.9	RDF feed (kg/s)	0.7	Niziolek et al. (2015b)
RWGS Reactor	3.19	2556	Feed (t/day)	0.65	Ordóñez et al. (2022)
MTO and OCP Reactors	65.73	86	Feed (t/h)	0.85	Hannula and Arpiainen (2015b)

Economic Data

Table B.21: Market prices, uncertain costs and taxes used in economic assessment. The values presented are on a 2023 monetary basis.

Item		Units	Value			Reference
			Minimum	Median	Maximum	
Market Data						
Methanol ¹		GBP/tonne	162	294	481	Polymer Update (2024)
Ethanol		GBP/tonne	273	453	877	Trading Economics (2024)
Ethylene ¹		GBP/tonne	330	980	1393	Polymer Update (2024)
Propylene ¹		GBP/tonne	322	1023	1398	Polymer Update (2024)
Uncertain Costs ²						
Offshore electricity ³	wind	GBP/MWh	59	64	72	BEIS (2023b)
CAPEX		%	50	100	150	Towler and Sinnott (2022b)
Taxes						
Landfill tax		GBP/tonne		102		WRAP (2024b)
Carbon tax		GBP/tonne		260		BEIS (2020b)

¹ Price alerts from Polymer Update accessed and compiled via the Factiva database (Dow Jones, 2024).

² Values used to construct triangular distributions.

³ Includes a 30% supplement required to give an uninterrupted supply (Nyhus et al., 2024b).

Life Cycle Inventories

Landfilling data

The environmental impacts of the landfilling route were taken directly from Ecoinvent v3.9. The process chosen as a proxy is the “Municipal solid waste CH— treatment of municipal solid waste, sanitary landfill — Cut-off, U” since there are no UK-specific processes in the database. The dataset consider landfill gas capture and utilisation, with the following assumption:

- Landfill gas capture and utilisation generates 0.043 kWh of electricity and 0.077 MJ of heat.
- Capture efficiency is 53%. Of the total landfill gas 47% is emitted, 18% is captured and flared, and 35% is captured and utilised.

Incineration data

The incineration route was assumed to have the same RDF facility before the incinerator as in the gasification routes, so a similar level of scrap and recyclable material is recovered before being sent to the incinerator. The net electricity and heat generated was calculated using efficiency data from the Runcorn incineration facility in the UK (Environment Agency, 2022), which generates 0.605 kWh of electricity and 1.944 MJ of heat per kg of waste fed to the incinerator.

Green H₂

Table B.22: Life cycle inventory data for green H₂ using offshore wind as the electricity source

Material/Energy Flow	Unit	Amount
Inputs		
Offshore wind electricity, UK	kWh	51.2 ¹
Water	kg	10.0 ²

¹ BEIS (2021b)

² Al-Qahtani et al. (2021)

MSW Routes

Table B.23: Life cycle inventory data for gasification, incineration and landfilling routes. Functional unit is 1 kg of MSW as received by the plant.

Flow	Unit	Amount							
		MeOH CCU	MeOH CCS	EtOH CCU	EtOH CCS	MTO CCU	MTO CCS	EFW	LDF
Inputs									
Green H ₂	kg	0.051	0.020	0.049	0.018	0.051	0.020		
Water	kg	0.121	0.121	0.121	0.121	0.121	0.121		
NaOH, 50wt% solution	kg					0.013	0.010		
Offshore wind electricity (base)	kWh	0.292	0.256	0.283	0.248	0.319	0.277		
Offshore wind electricity (heating)	kWh	0.056		0.653	0.408	0.075	0.014		
Offshore wind electricity (cooling)	kWh	0.083	0.065	0.110	0.085	0.075	0.112		
CO ₂ transport and storage ¹	kg		0.259		0.259		0.259		
CO ₂ (product credits)	kg	0.553	0.421	0.531	0.405	0.507	0.385		
CO ₂ (storage credits)	kg		0.157		0.157		0.157		
Avoided Products									
Methanol	kg	0.666	0.507						
Ethanol	kg			0.460	0.350				
Ethylene, naphtha cracking	kg					0.118	0.089		
Propylene, naphtha cracking	kg					0.149	0.114		
Grid electricity, UK	kWh							0.484	0.043
Heat, natural gas	MJ							1.555	0.077
Outputs - Emissions									
Carbon dioxide (to air)	kg	0.036	0.021	0.044	0.028	0.062	0.042		
Outputs - Waste Treatment									
Wastewater, average	kg	0.439	0.346	0.622	0.486	0.802	0.621		
Inert waste, sanitary landfill	kg	0.132	0.132	0.132	0.132	0.132	0.132	0.100	1.000
Glass, recycling ²	kg	0.050	0.050	0.050	0.050	0.050	0.050	0.050	
Aluminium, recycling ²	kg	0.025	0.025	0.025	0.025	0.025	0.025	0.025	
Iron and steel, recycling ²	kg	0.025	0.025	0.025	0.025	0.025	0.025	0.025	
MSW incineration, UK	kg							0.800	

¹ Using inventory data provided by Terlouw et al. (2021b) for CO₂ transport and geological storage using a 200km pipeline.

² Cut-off methodology means no impacts for recycled material retrieved from the RDF facility, but these are included in the LCI data to close the mass balance.

Monetisation Factors

Table B.24: Monetisation factors for endpoint environmental impacts (Weidema, 2015a). Values adjusted to GBP on a 2023 basis to match break-even gate fee units.

Endpoint	Units	Value [GBP2023]
Human health	DALY	1.35×10^5
Ecosystem Quality	species.yr	3.61×10^7
Resource Depletion	GBP2023	0.98

Midpoint Results

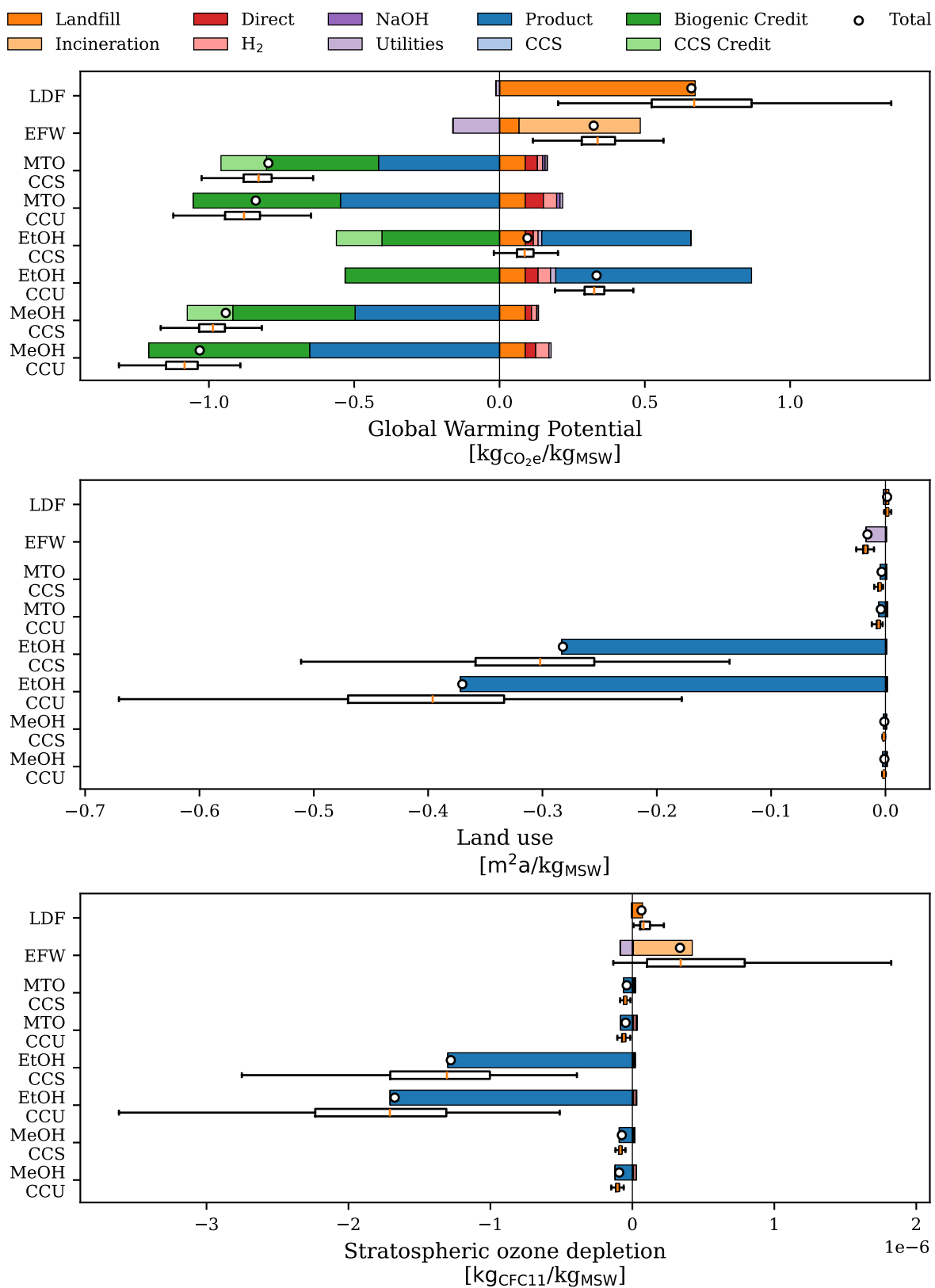


Figure B.9: Midpoint results (1/6)

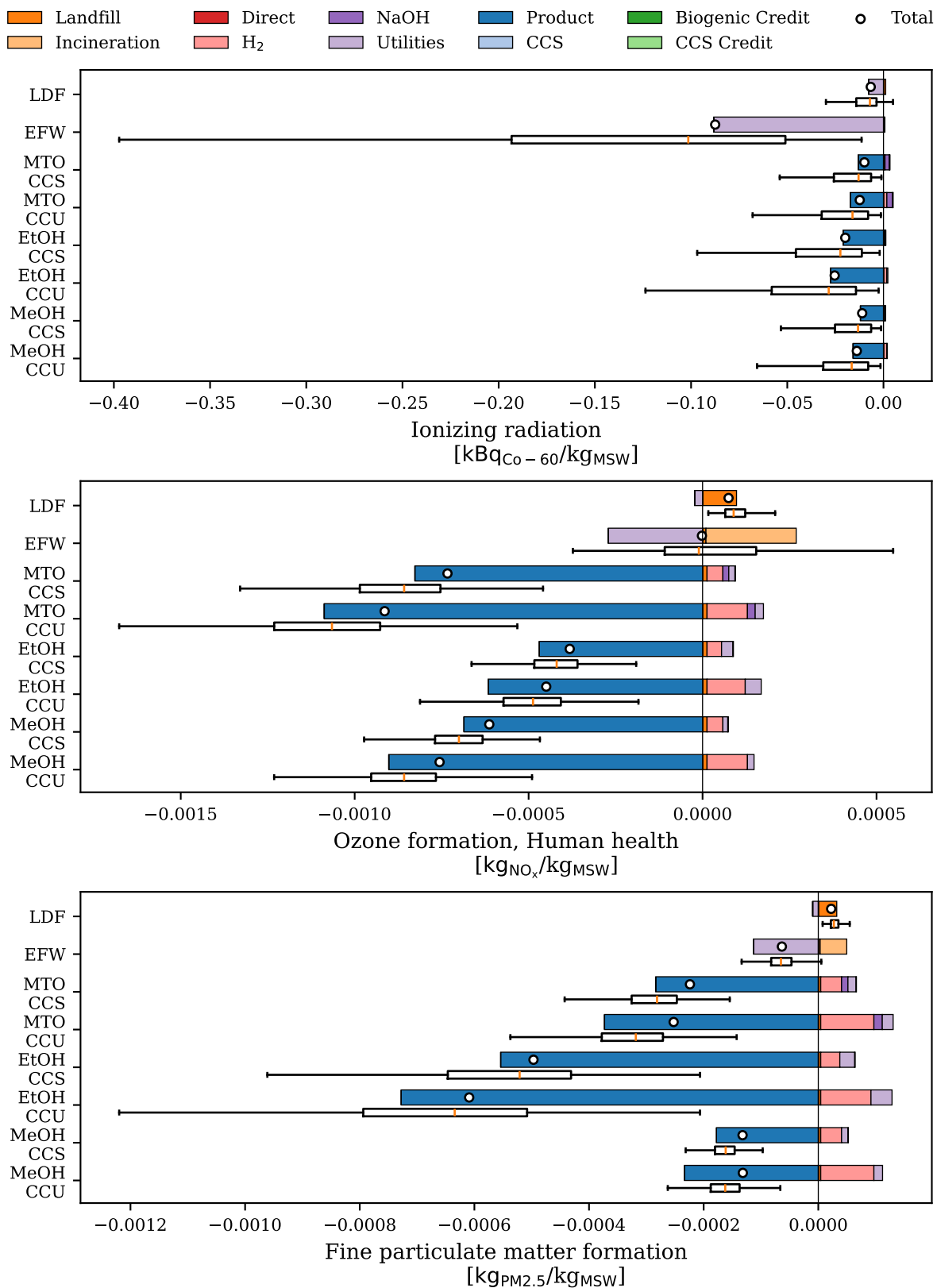


Figure B.10: Midpoint results (2/6)

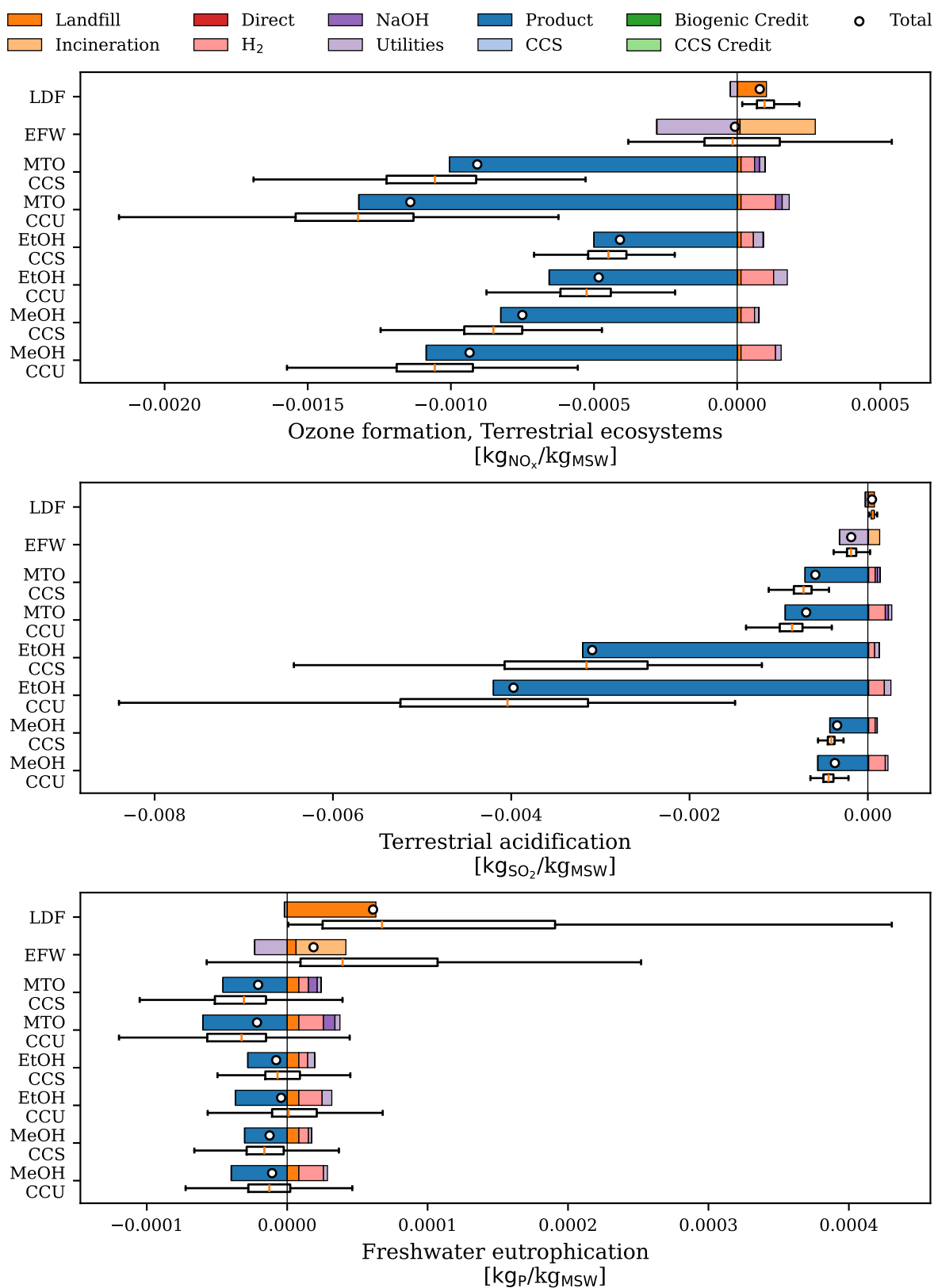


Figure B.11: Midpoint results (3/6)

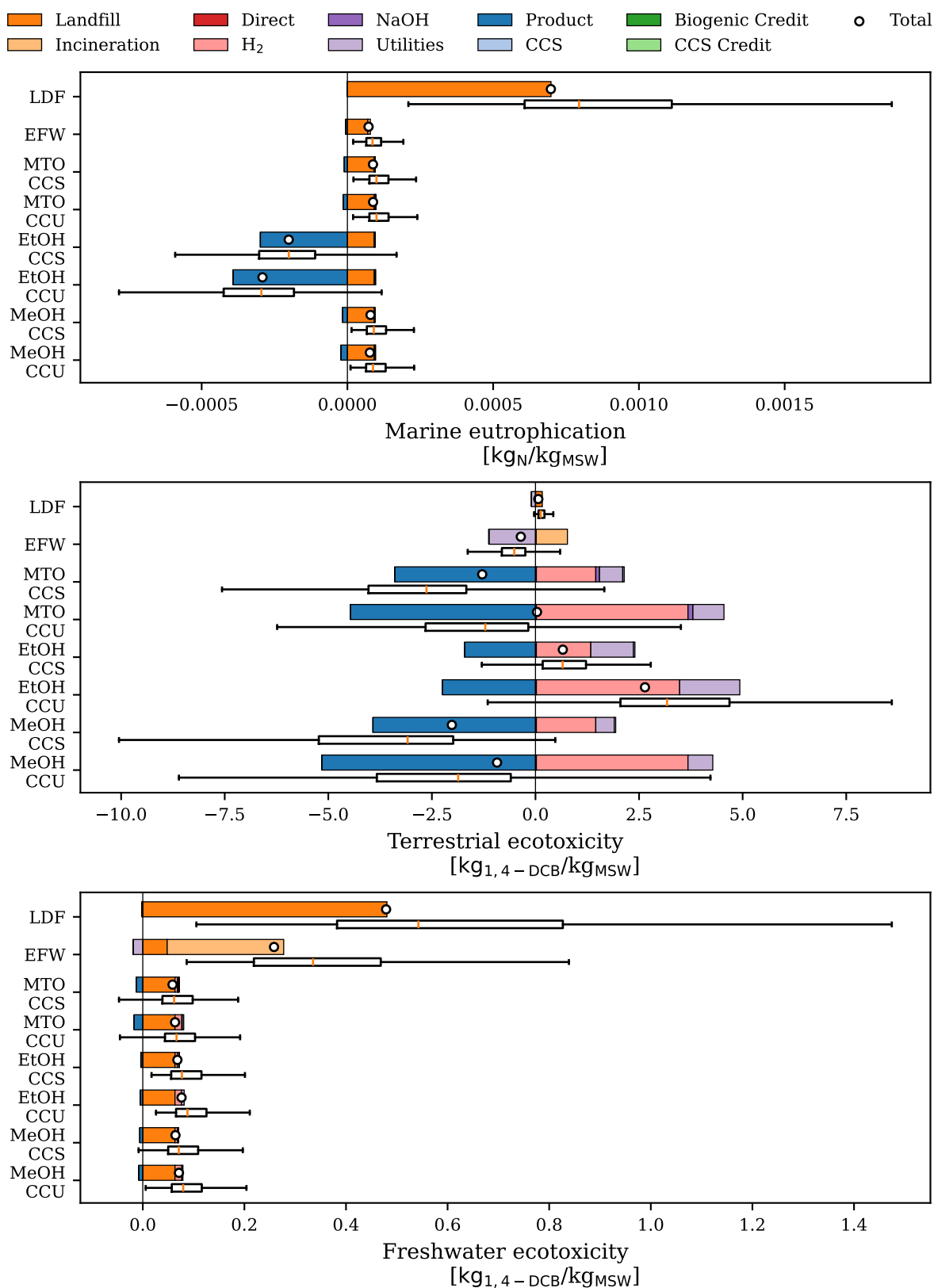


Figure B.12: Midpoint results (4/6)

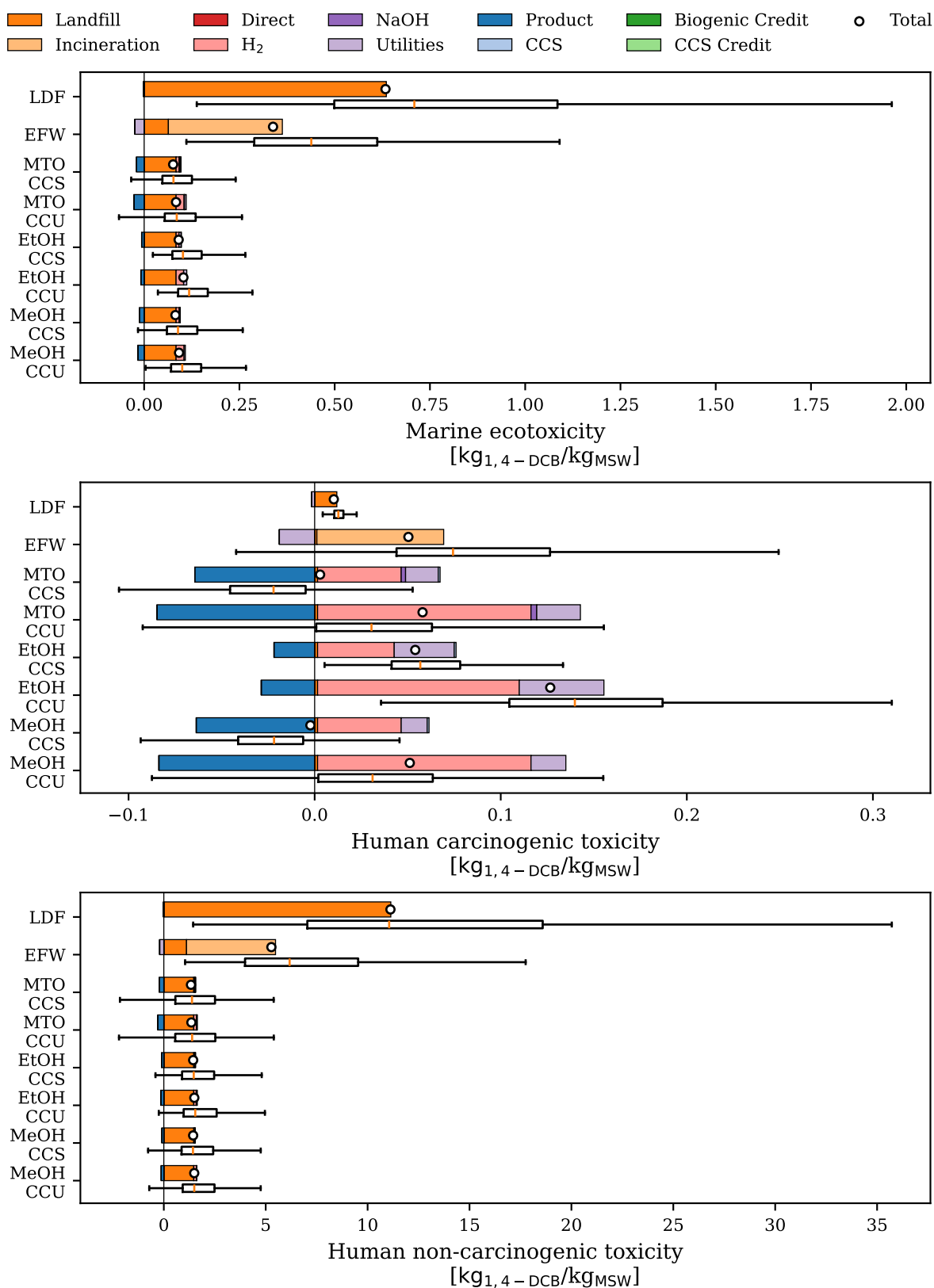


Figure B.13: Midpoint results (5/6)

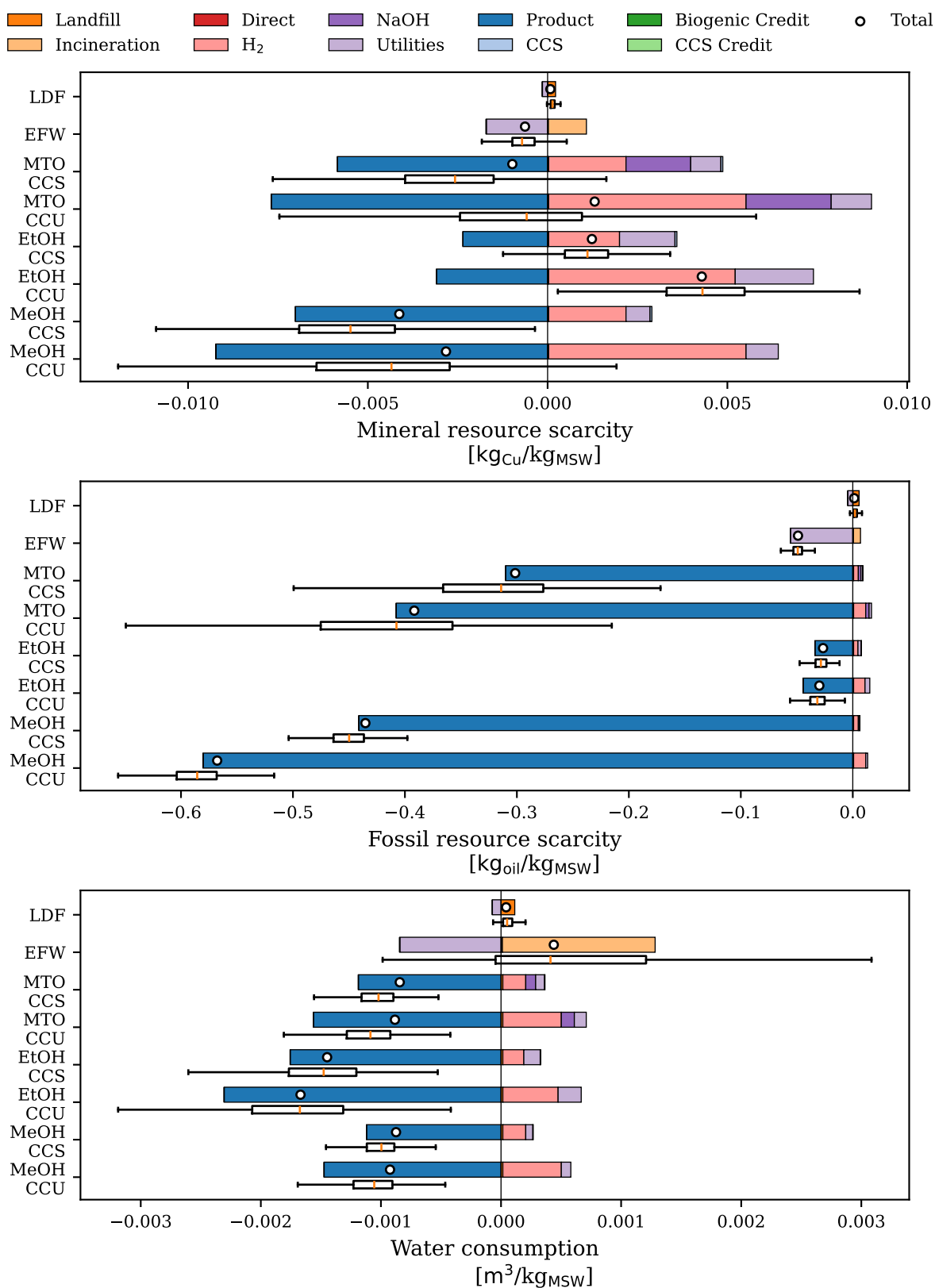


Figure B.14: Midpoint results (6/6)

Endpoint Results

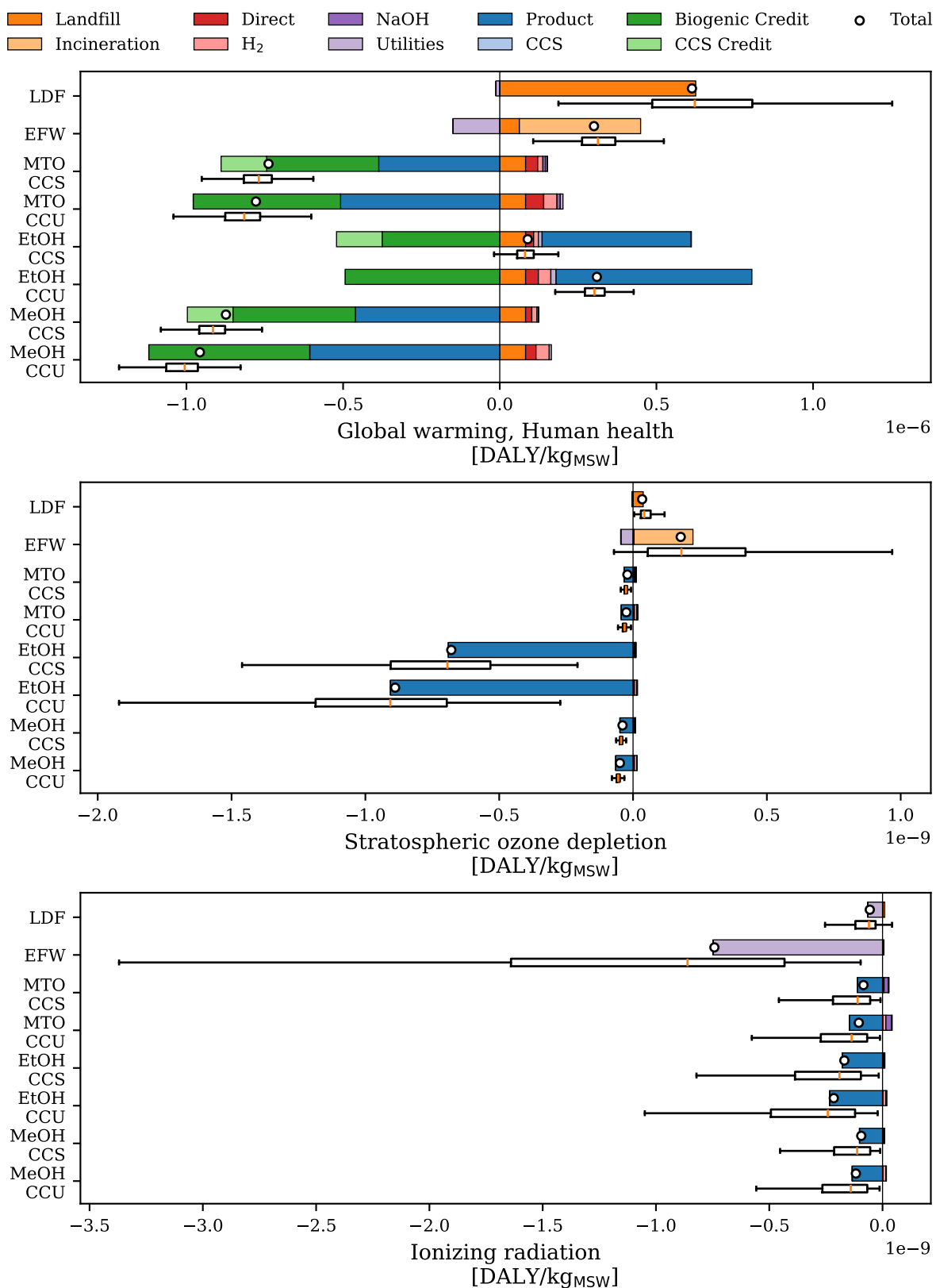


Figure B.15: Endpoint results (1/8)

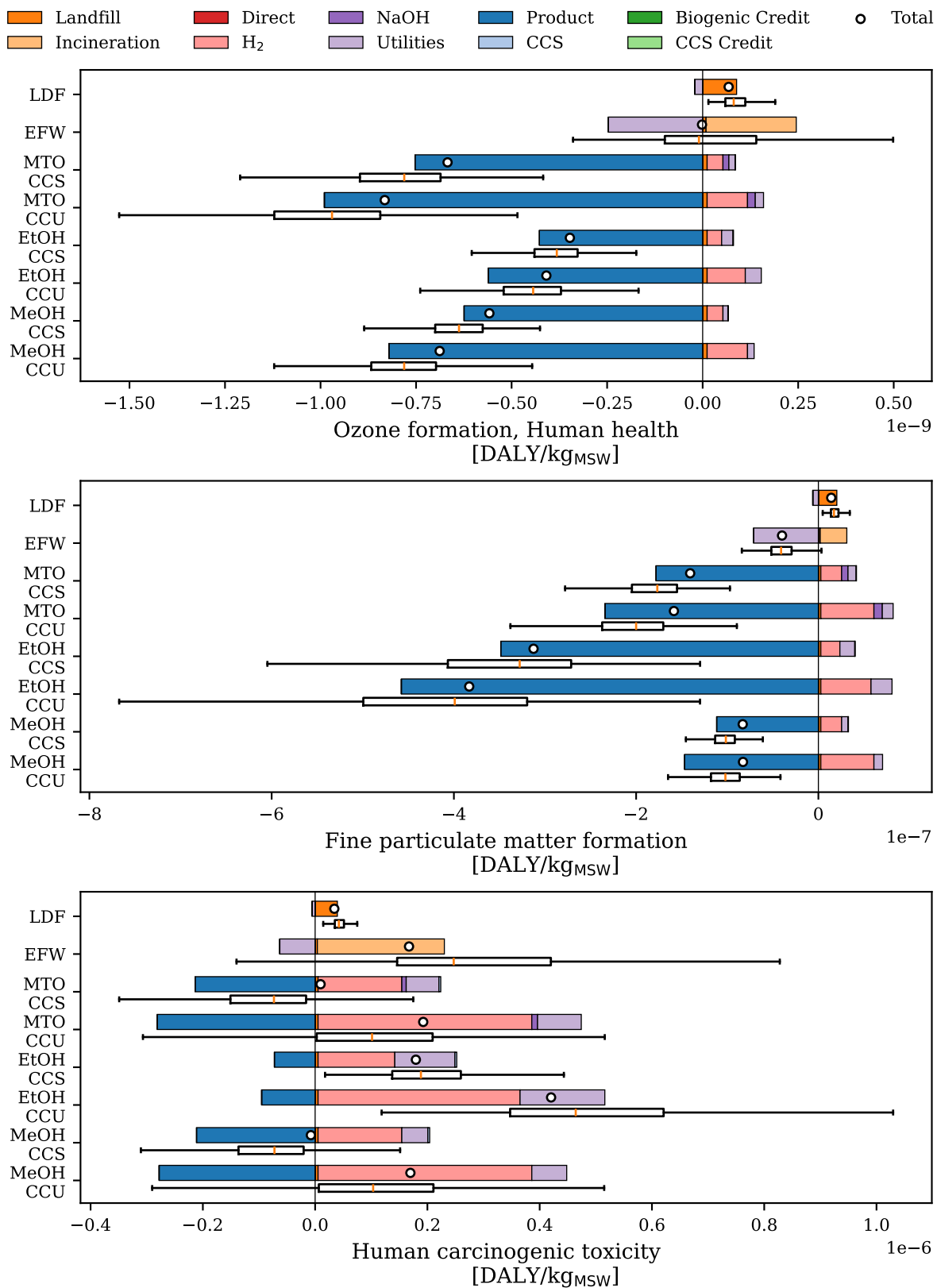


Figure B.16: Endpoint results (2/8)

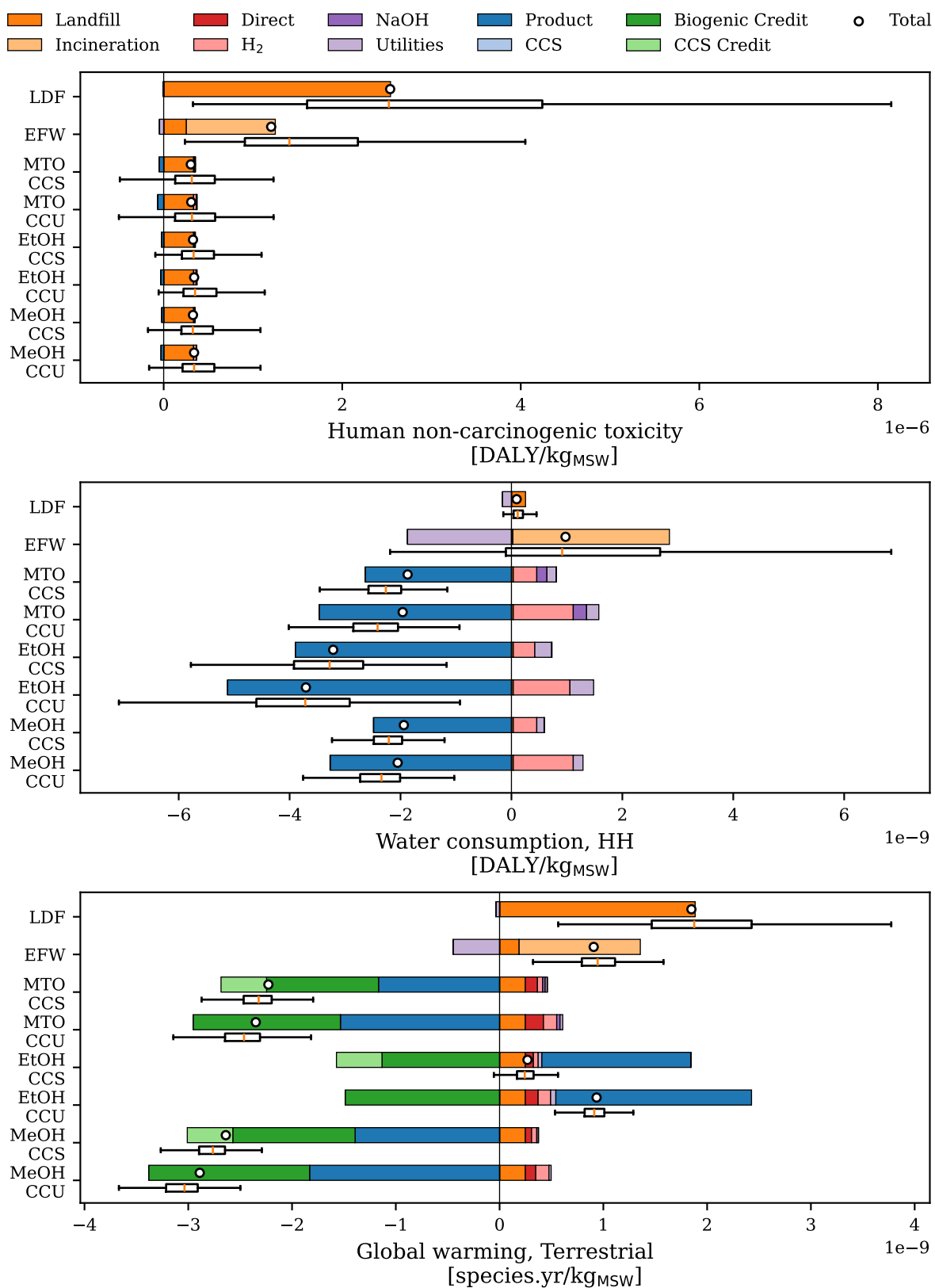


Figure B.17: Endpoint results (3/8)

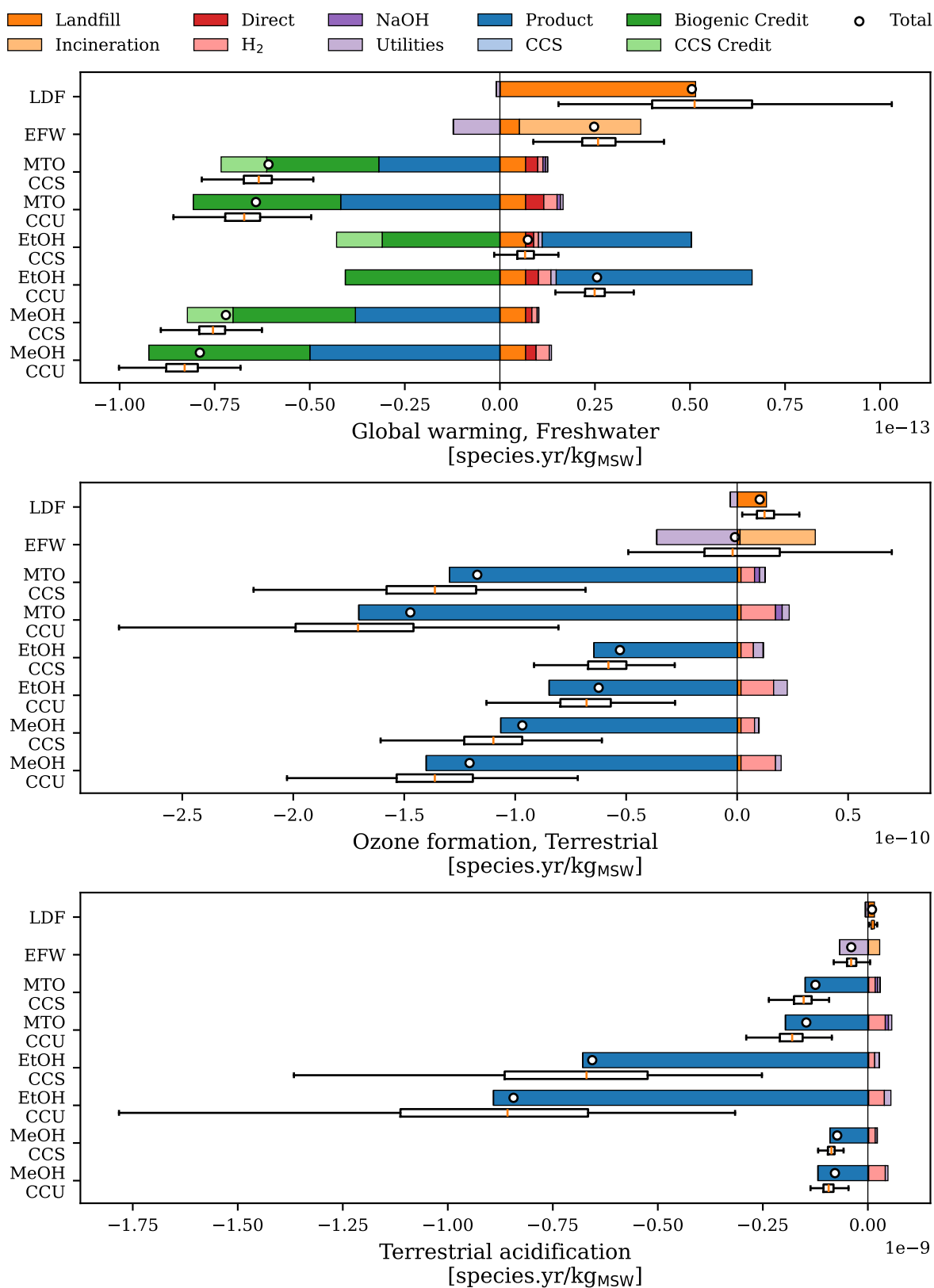


Figure B.18: Endpoint results (4/8)

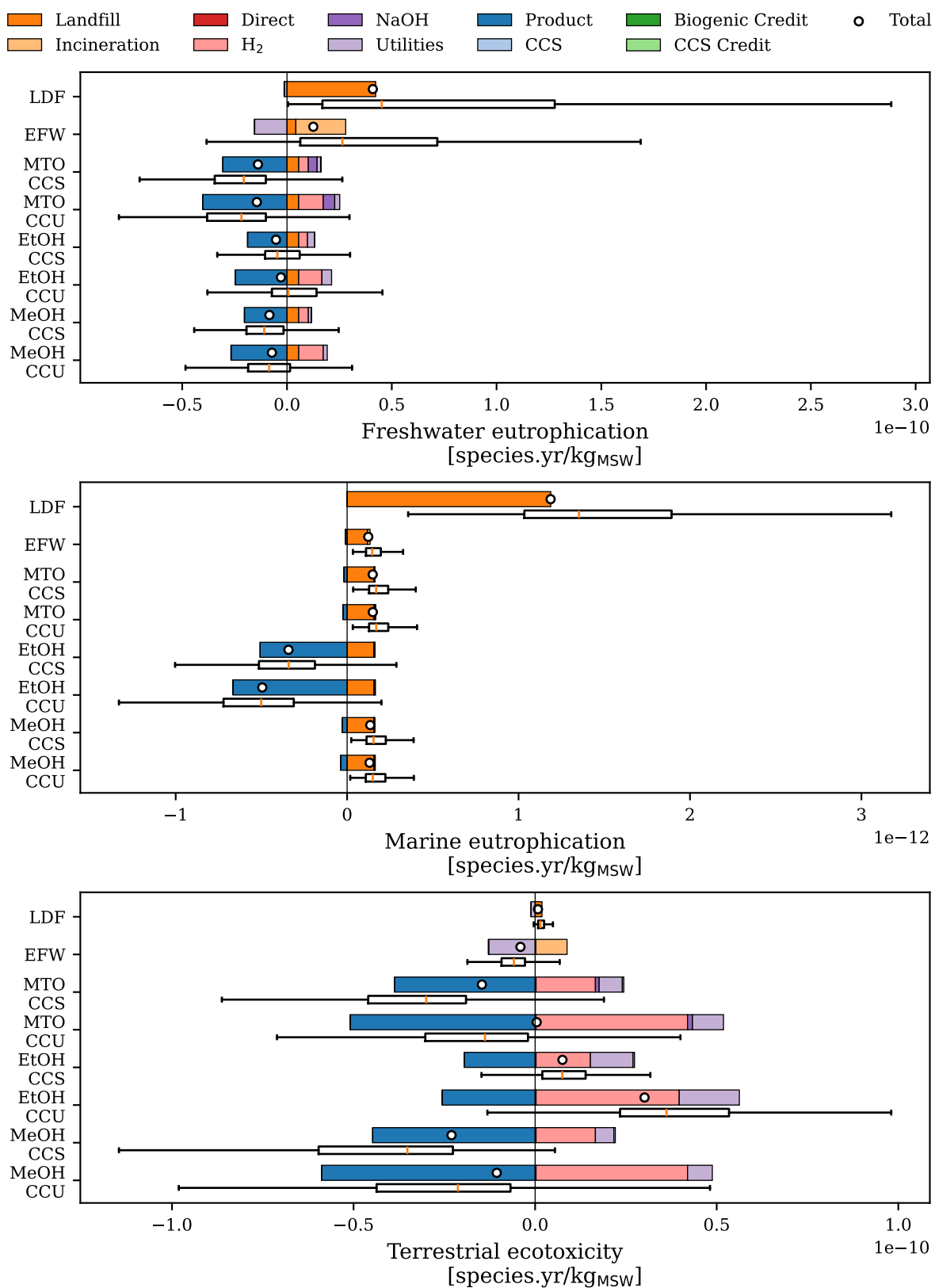


Figure B.19: Endpoint results (5/8)

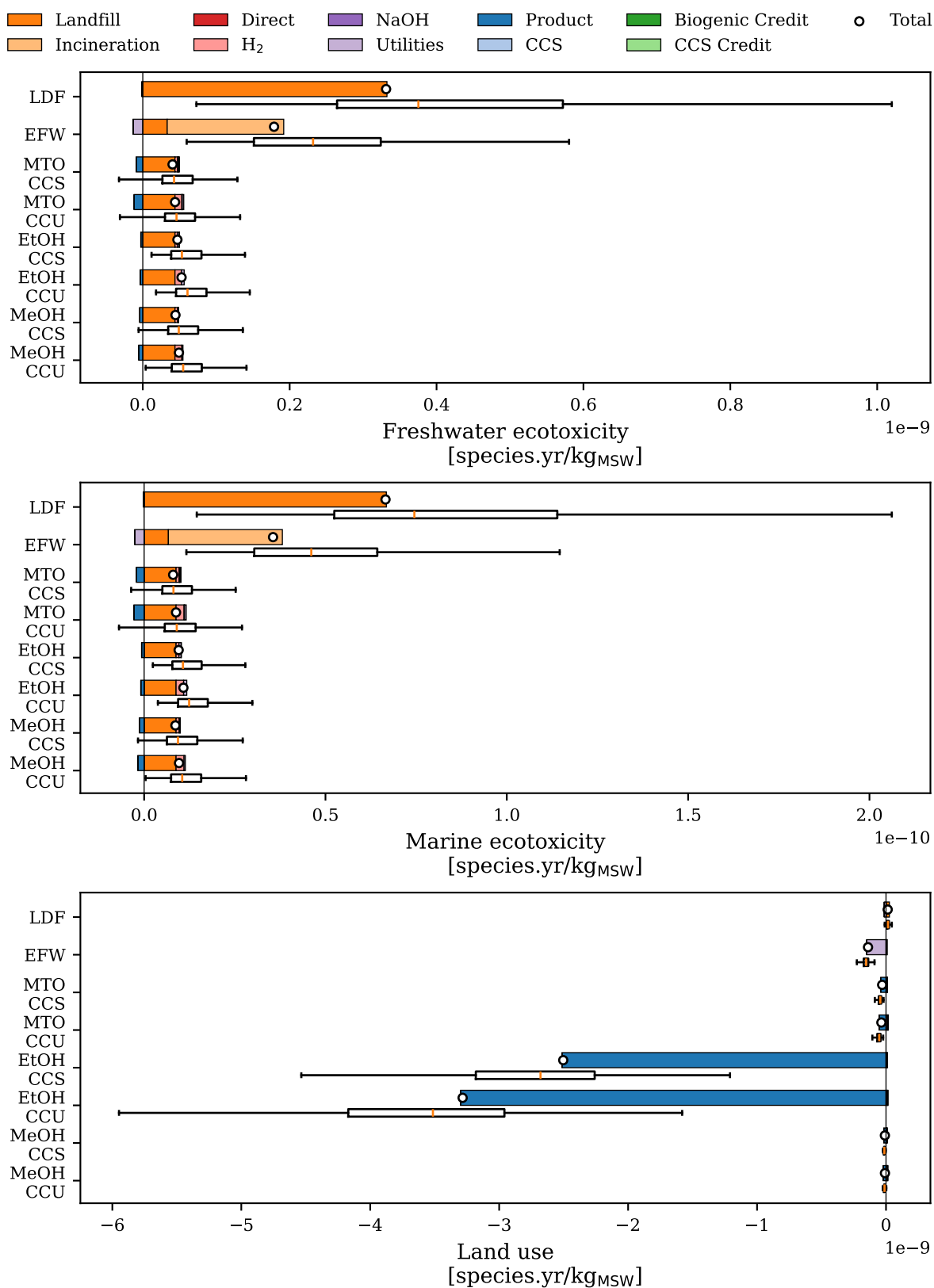


Figure B.20: Endpoint results (6/8)

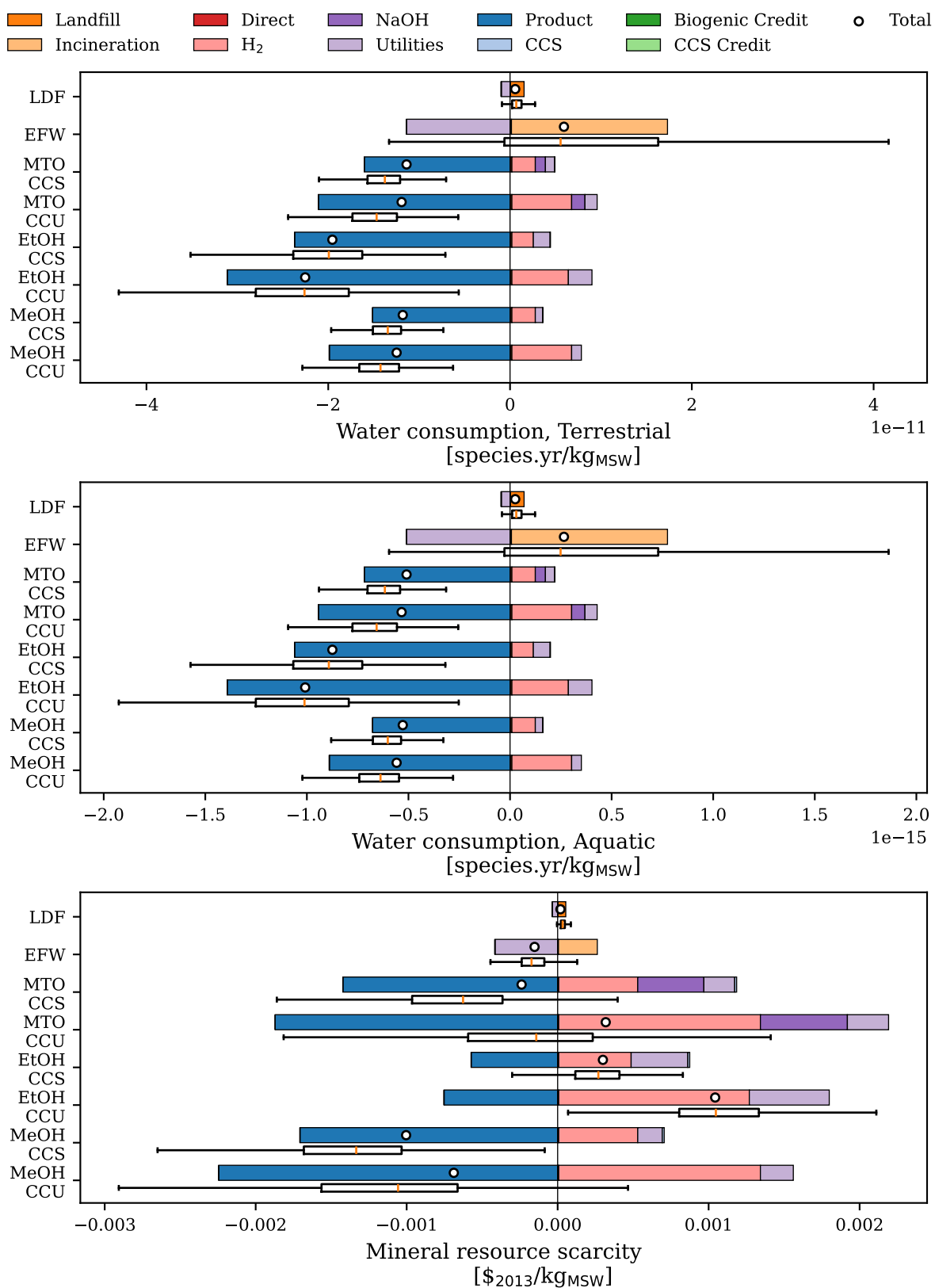


Figure B.21: Endpoint results (7/8)

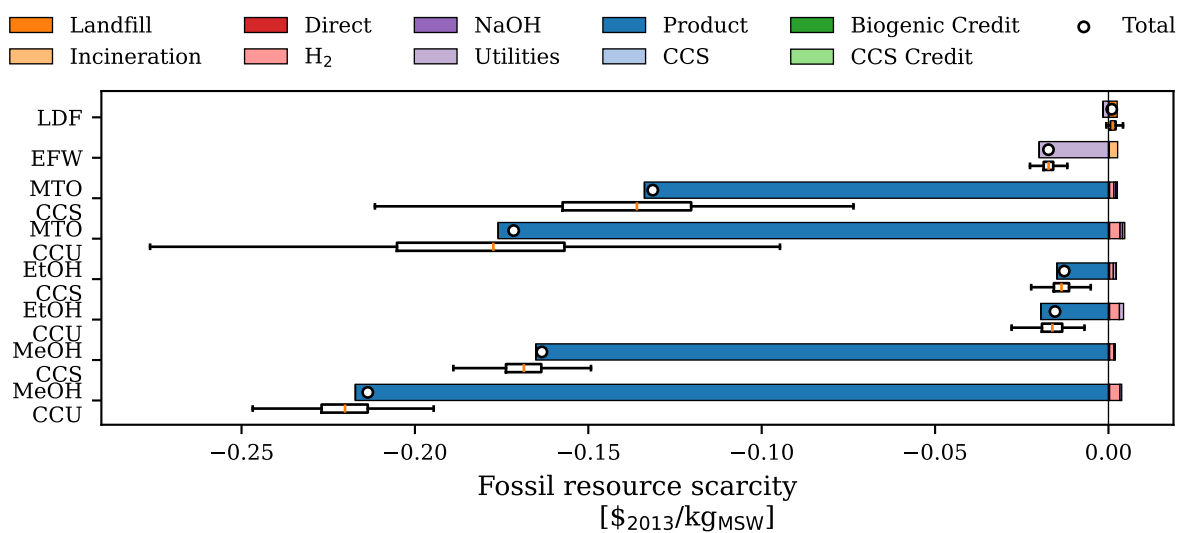


Figure B.22: Endpoint results (8/8)

Waste Composition Variability - EEC Breakdown

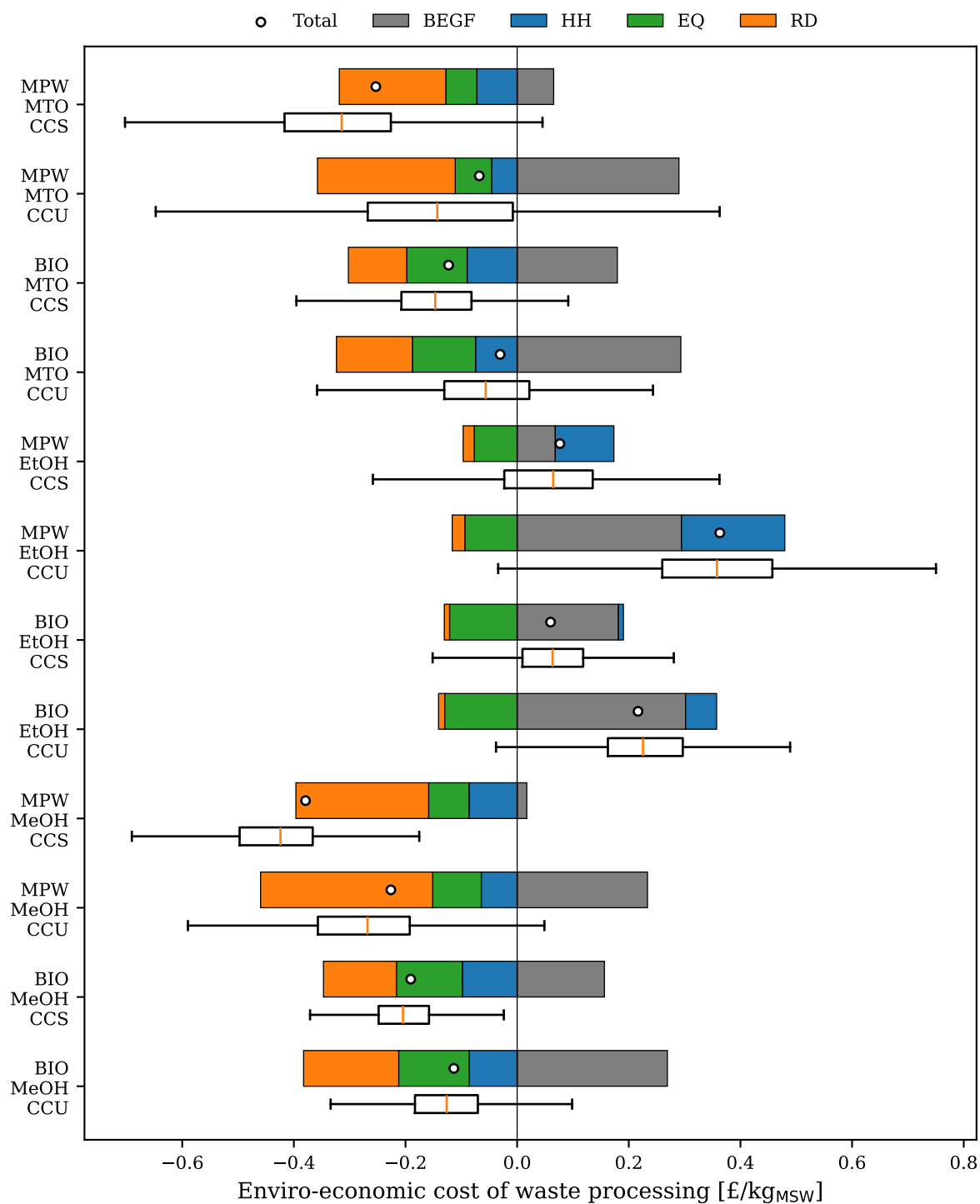


Figure B.23: EEC Breakdown for both BIO and MPW feedstocks.

Appendix C

Direct CO₂-to-Ethanol Synthesis

Route Descriptions

Co-fed Methanol-Ethanol Dehydration

The overall configuration of the co-fed methanol-ethanol dehydration plant is similar to that of the MTO process, and is summarised in Figure C.1. First, the methanol-ethanol feed is pumped and heated to 1.5 bar and 470°C, respectively. It is then fed to an isothermal packed bed reactor filled with an HZSM-5 methanol-to-propylene catalyst (R-100). This catalyst benefits from low coke formation at 0.2wt%, but still requires three reactors in parallel during operation so that they can be regenerated (Koempel and Liebner, 2007; Schulz, 2010). In Aspen HYSYS, this was modelled with a yield shift reactor, where the product distributions were interpolated from experimental results depending on the methanol to ethanol feed ratio (Feng et al., 2020). An assumption made was that the C5+ alkene products were an equal split ranging from C5 to C10 (Rodríguez-Vallejo et al., 2020). After the main reactor, the product mixture is sent to a recirculating water quench tower (T-100), which cools the products and removes approximately 90% of the produced water.

Next, a three-stage compression train with interstage cooling compresses the products up to 18 bar. At each stage of this compression train, a three-phase separator is used to remove any condensed water and higher alkenes. For the olefin separation section, a

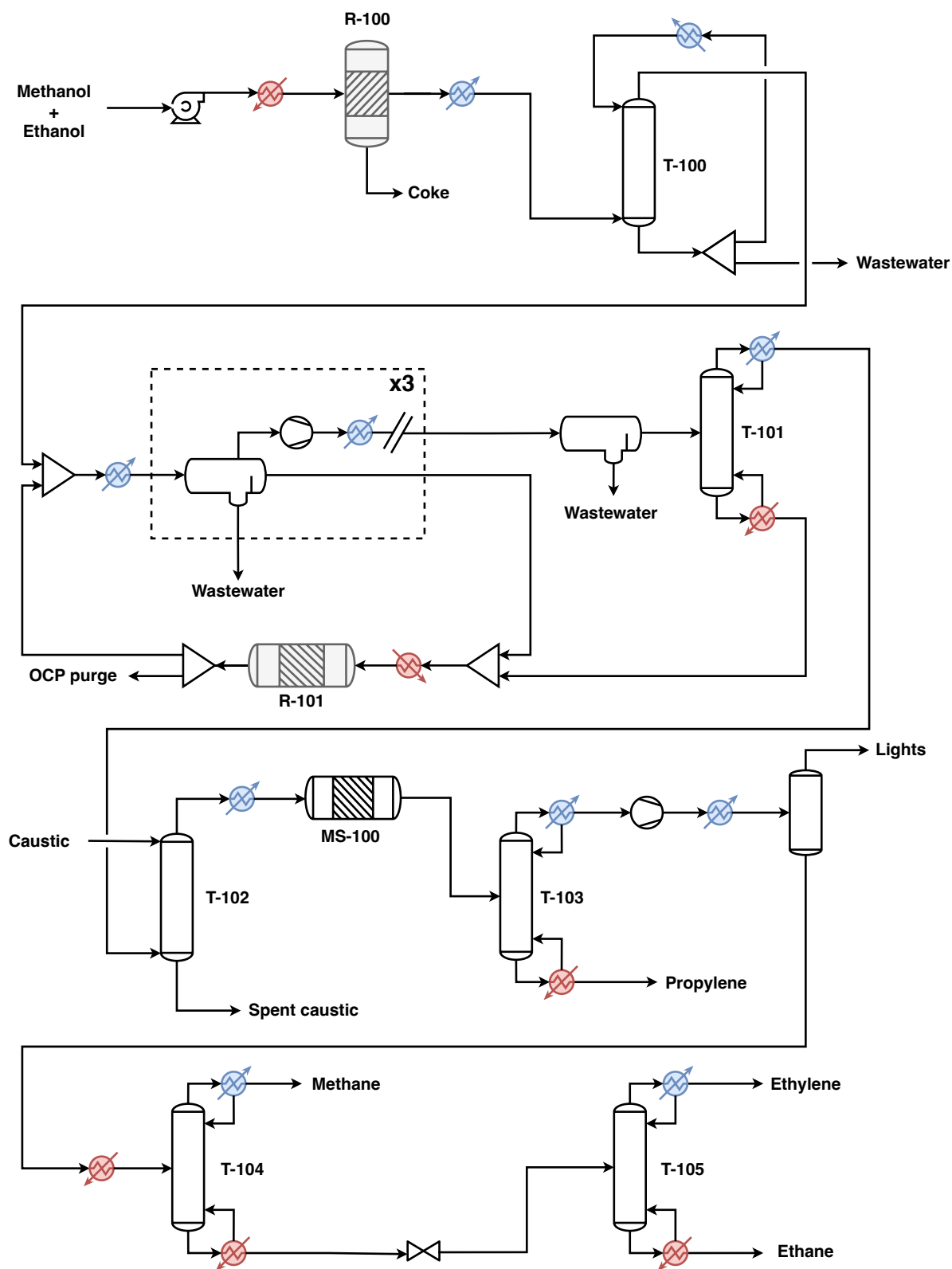


Figure C.1: Process flow diagram for co-fed methanol-ethanol dehydration to olefins.

depropaniser front-end configuration is used (Zimmermann and Walzl, 2009), where the C₄+ hydrocarbons are separated in the bottoms, whilst the C₂s, C₃s and light gases are

removed from the top of the column (T-101). The top products are then sent to a caustic wash column (T-102) with NaOH solution to remove the CO_2 down to 1ppm. This is followed by passing the stream through a molecular sieve (MS-100) to remove any final traces of water as a pre-requisite for the subsequent cryogenic distillation columns. The now predominantly C2/C3 stream is sent to a de-ethaniser column (T-103), where the propylene product is recovered from the bottoms. Note that propane formation was not considered in the experimental data used in the reactor for this model, so a C3 splitter column was not required. The top product was then compressed to 40 bar, and cooled to -94°C to remove some of the light gases (i.e. H_2 and CH_4). The final two columns in the separation section are the demethaniser (T-104), which removes the final CH_4 from the tops, and a C2 splitter (T-105), which recovers the ethylene from the ethane.

Similar to an MTO plant, an olefin cracking process (OCP) is included to convert the higher alkenes to additional ethylene and propylene (Vora and Pujado, 2010). In the METO plant, the C4+ by-products from the bottom of the depropaniser and the C5+ alkenes recovered from the three-phase separators in the compression train are fed to the OCP reactor (R-101). This is modelled as a Gibb's reactor in Aspen HYSYS at 500°C , and the produced ethylene and propylene are then cooled and recycled back to the start of the compression train.

Additional Results

Green Premium with Base Case

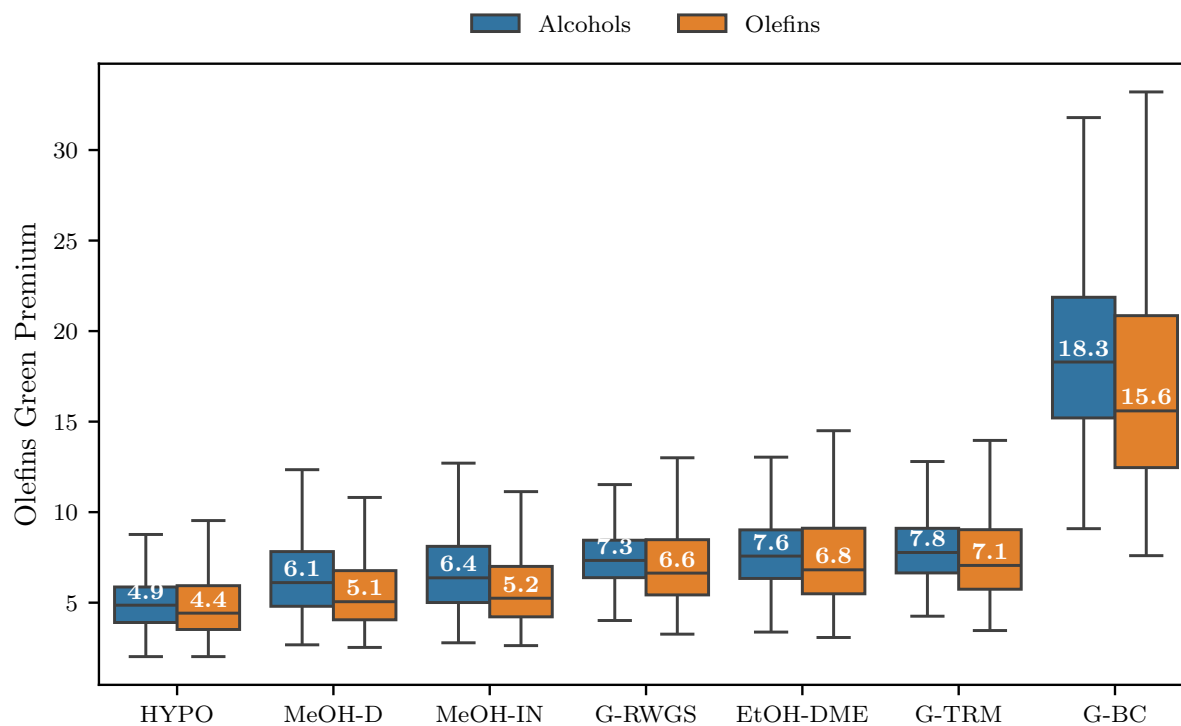


Figure C.2: Green premium distributions for alcohol and olefin production for the best performing version of each route type. Median values are highlighted within each box plot.

Separate vs Co-fed Dehydration GP

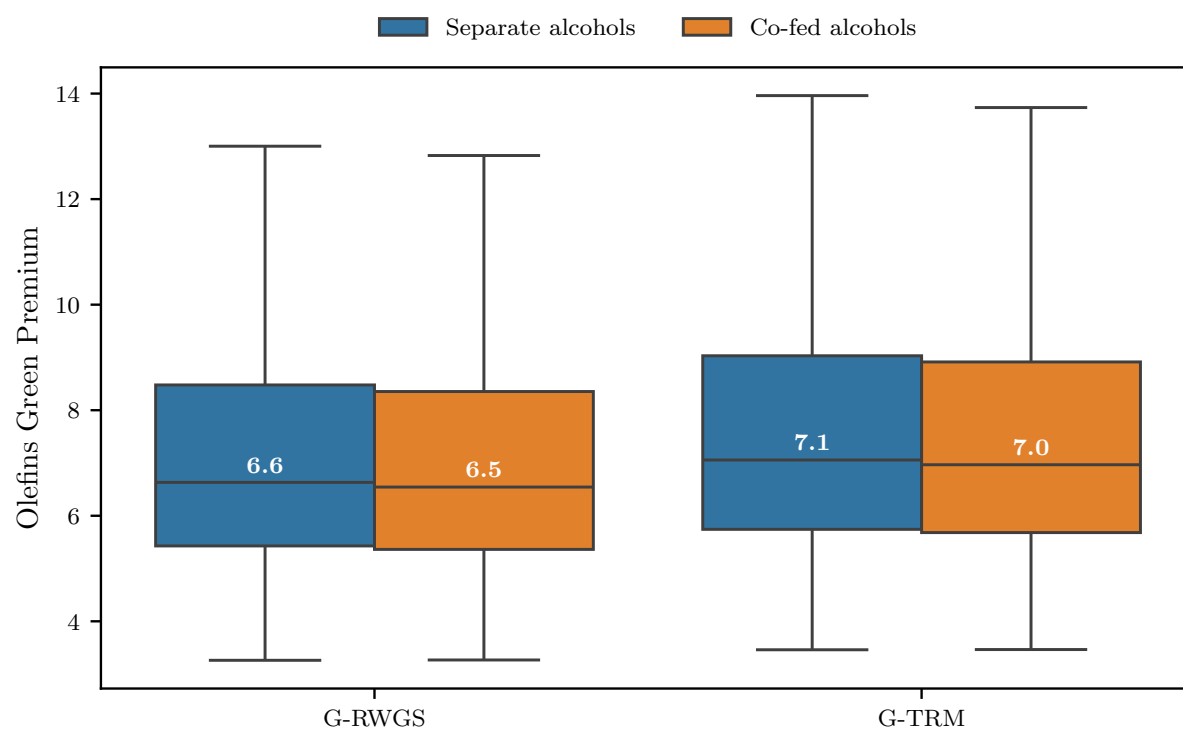


Figure C.3: Olefin green premium distributions for G-RWGS and G-TRM comparing a separate and co-fed olefin production facility.

Appendix D

Methane Side Stream Valorisation

Life Cycle Inventories

Table D.1: Life cycle inventories for OCM and TRM routes.

Mass/Energy Flow	Unit	OCM	TRM
CO ₂ feed	kg		0.14
Water feed	kg		0.06
O ₂ feed	kg	1.93	0.90
CH ₄ substitution	kWh	12.51	12.51
Wastewater	m ³	1×10^{-3}	5×10^{-5}
Methanol	kg		1.95
Ethylene	kg	0.50	
CCS	kg	0.90	
Electricity (Direct)	kWh	0.80	0.94
Electricity (Cooling)	kWh	0.52	0.13
Direct CO ₂ emissions	kg	0.13	0.20