Sustainable Energy & Fuels

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
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Cite this: *Sustainable Energy Fuels*, 2025, **9**, 4660

Prospective techno-economic assessment of carbon capture & utilization and biobased processes for methanol and ethanol production†

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A sustainable future will require a phase-out of fossil-based resources if we want to reduce greenhouse gas emissions. However, trade-offs occur between costs, energy use, and CO_2 emissions or land use. Choosing between different fossil-based, biobased and CO_2-based routes requires knowledge of these parameters. We evaluated chemical methanol and microbiological ethanol production routes from different feedstocks (sugar, side-streams, CO_2 and biogas) under a prospective 2050 scenario to determine future scenarios that would allow for the use of alternative routes. Conventional routes for methanol and ethanol production showed the lowest production costs. The highest costs in the alternative methanol and ethanol routes based on CO_2 are associated with the conversion of CO_2 to the more reactive, hydrogen-enriched syngas. The CO_2-based routes require large amounts of renewable energy. The biogas alternatives require less energy, but show higher CAPEX and raw material costs. To enable complete comparison to fossil-based production, ethanol results were extrapolated to ethylene production. The subsequent scenario analysis indicated that non-fossil methanol and ethylene production should be feasible from an economic point of view when carbon taxes are applied, starting from around 100 € per ton CO_2 for methanol and 270 € per ton CO_2 for ethylene production routes. For both bioethanol and bioethylene production, the 1st and 2nd generation processes are limited by the amount of available land to grow the crops. In the end, there are multiple variables that influence the feasibility of the alternative routes. A combination of technology development, market price development and governmental measures can allow for cost parity.

Received 27th March 2025
Accepted 2nd July 2025

DOI: 10.1039/d5se00435g

rsc.li/sustainable-energy

1 Introduction

Currently, fossil-based sources dominate as the primary providers of energy and carbon. The production of fuels and other products, such as chemicals and polymers, is a highly integrated industry in which fossil feedstocks are converted into a wide range of products. Fuels account for the largest share of this, requiring roughly 80% of the currently used fossil feedstocks.[1]

By operating at a large scale and producing a wide range of products, the petrochemical industry can produce both fuels and chemical products at low costs. However, the use of fossil-based feedstocks causes pollution and is the main cause of greenhouse gas emissions.[2] To address these challenges, alternative renewable resources must be explored, and advanced technologies must be developed to enable the sustainable production of energy, carbon-based chemicals, and materials. The European Union has set a goal to achieve carbon neutrality by 2050, necessitating the gradual elimination of fossil fuels in chemical production.[1]

Renewable energy alternatives, such as solar, wind, hydro, and nuclear energy, can produce electricity, but do not provide the carbon required to produce chemicals and materials. In a fossil-free future, methanol and ethanol are anticipated to serve as crucial platform chemicals, with their demand expected to increase significantly.[3–6] Therefore, this study focuses on the production of methanol and ethanol, as these could serve as potential platform chemicals to produce a wide variety of chemicals and materials. More specifically, methanol is viewed as a valuable component in the chemical industry, as it can be used as a fuel, solvent, and chemical building block.[7] Currently, the main source to produce methanol is natural gas (CH_4), which is chemically converted to syngas using methane steam reforming and subsequently converted into methanol. Ethanol is already widely used as a fuel and has great potential as a chemical building block. It can, for example, be converted to ethylene,[8] which can subsequently be used in the production of a large variety of chemicals and materials.[9,10] Currently, ethanol

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† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d5se00435g

is mainly produced from beet or cane sugar or starch *via* fermentative processes.[11]

In a fossil-free scenario, carbon can be sourced from biomass, CO_2, or recycling streams. Biomass can be obtained from primary crop sources that produce starch or sugar, or from secondary sources such as crop residues (*e.g.* sugarcane bagasse or corn stover). For comparison, routes using CO_2 from point sources (*e.g.* biogas production or waste incineration) or from direct air capture are studied. Recycling of materials is an important third route.[12] Although material recycling is an important approach, it is more relevant for polymer production and is therefore excluded from this analysis, which centres around methanol and ethanol.

Several studies have reviewed the potential of Carbon Capture and Utilization (CCU),[13–15] and recent perspective papers have explored the possibilities of a future refinery that does not consume fossil feedstocks but uses (plastic) waste, biomass or CO_2 as feedstocks.[1,16] These studies typically focus on technology but lack an economic perspective. There are a few studies that performed a techno-economic assessment (TEA) on alternative CO_2-based routes for methanol[7,17–19] or ethanol production.[20] However, these studies focus on different aspects of the production of methanol and ethanol, and therefore, the results of these studies are difficult to compare with each other. One TEA study compared CO_2-based routes to both ethanol and methanol within one paper,[11] and another study more generally evaluated CO_2 use for chemicals.[21] The latter identified ethanol as the most suitable chemical to be produced from CO_2. To address this, this study aims to provide more information on the trade-offs of different biobased/CO_2-based routes for the production of methanol and ethanol.

This study analyses, evaluates, and compares chemical and microbiological methanol and ethanol production routes from different feedstocks (sugar, side-streams, CO_2 and biomethane) under a prospective 2050 scenario. It uses available literature on the technologies that are needed for these routes. The findings highlight the performance of different methanol and ethanol production routes, in terms of costs, energy use, and CO_2 emissions or land use. Subsequently, the CO_2 tax, energy and raw material costs were varied to calculate the cost parity of the alternative routes. We emphasize the significance of this comparison in the context of reducing greenhouse gas emissions and transitioning away from fossil-based resources. This work aims to identify key trade-offs between economic, environmental, and land-use factors illustrated by the use cases for ethanol, ethylene and methanol, and to identify the bottlenecks of the processes studied.

2 Approach

Different processes for methanol and ethanol production were selected based on their technology readiness level (TRL), carbon efficiency, and energy efficiency. The conventional routes reflect current industry practices, while alternative routes were selected to represent technological developments that are likely to mature within the next 25 years. Each process was individually evaluated using its corresponding mass balances and techno-economic parameters. Subsequently, these individual processes were combined to evaluate the different methanol and ethanol production routes.

2.1 Techno-economic assessment

The techno-economic assessment (TEA) estimated the operational expenditures (OPEX) and capital expenditures (CAPEX) of each unit operation based on literature values and data from SuperPro Designer. Mass balances were calculated in Excel to link the different unit operations with each other in order to calculate the requirements and performance of each route. The total production cost for each route, expressed in € per ton of product, was calculated as the sum of the annualized CAPEX, raw material, electricity, high temperature (HT) heat, and low temperature (LT) heat costs. A more detailed overview of CAPEX, OPEX and input for mass balances of each unit operation can be found in Appendices A and B.†

All processes, except for anaerobic digestion (AD), which is typically employed as a small-scale local solution, were scaled to large production size to minimize production costs as a result of economy of scale. For most equipment, CAPEX scales with a power factor of 0.6. For the technologies DAC, H_2O-electrolysis, and co-electrolysis, CAPEX scales linearly. The estimated CAPEX, including scaling factors, was based on literature. The chosen plant sizes and estimated CAPEX can be found in Appendix A.† The plant sizes were assumed to represent the maximum capacity for a given region, *i.e.* a further increase of production capacity would require construction of additional plants in a different region. Thus when multiple plants are required, CAPEX scales linearly with production capacity. All processes are assumed to operate 8000 production hours per year, except sugar cane processing which operates 200 days per year[22] and anaerobic digestion which operates year round, *i.e.* 8760 hours per year.

Annualized CAPEX was set to 20% of the total CAPEX per year. This percentage is roughly made up of 10% maintenance and overhead costs per year and 10% deprecation or financing costs per year. The Chemical Engineering Plant Cost Index (CEPCI) was used to translate CAPEX of equipment from a past date to current date based on inflation and deflation. The CEPCI value used in this study was 800 (2023 value), and the used US dollar-Euro exchange rate was 0.92 € per USD (2023 value).

Natural gas, sugar cane, corn stover, and AD feedstock mixture are the raw materials in this assessment. The used price for natural gas is 200 € per ton (4 USD per Mcf), which corresponds to the price in the Henry Hub (Louisiana), which is a distribution hub of natural gas, in 2018–2022.[23] The used Brazilian sugar cane (30% DW) price was 20 € per ton fresh weight (FW).[22] The US corn stover (70% DW) price was estimated to be 80 € per ton FW.[24] The AD feedstock mixture is assumed to consist of maize silage (35% DW) and cattle slurry (10% DW) that contribute 42% and 58%, respectively, to the amount of biogas produced.[25] This results in a FW ratio of 10% maize silage and 90% cattle slurry. With a price of 76 € per ton FW for maize silage[26] and a price of 1 € per ton FW for cattle slurry based on the estimated handling and transportation

costs,[27] this results in a price of 8 € per ton FW for the AD feedstock mixture.

Energy costs were divided into three categories: electricity, HT heat (>250 °C), and LT heat (<250 °C). Electricity and HT heat are regarded as a high-cost energy source with a price of 50 € per MWh, based on the current (2022) costs for solar energy production.[28] LT heat was assumed to cost 20 € per MWh. It is assumed that in the future the energy sources are renewable, and therefore have no CO_2 emission. Solar energy was used as the renewable energy source in this study to facilitate comparison between required surface area for electricity production and growing crops. However, wind energy could have been used as a renewable energy source, with on-shore wind energy being less expensive than solar energy and off-shore energy being more expensive than solar energy.[28]

2.2 Land use

For ethanol production, the required land use is estimated based on the required land use for growing crops, and/or the production of energy *via* solar panels. The average sugar cane yield in Brazil over 2018–2022 is 74 ton FW per (ha year).[29] The used maize silage yield is 45 ton FW per (ha year).[30] The required land-use for corn stover is based on the yields of maize and corn stover and their economic allocation. Based on an average yield of 10.9 ton FW per (ha year) for maize (85% DW) in the US over 2018–2022, the yield of corn stover (70% DW) is estimated based on 8.6 ton DW per (ha year).[31] Using a maximum sustainable removal rate of 68% for corn stover[24] and a price of 204 € per ton FW for maize,[26,32] results in an economic allocation of 77% for maize and 23% for corn stover. This subsequently leads to an economically allocated required land use of 36 ton FW per (ha year) for corn stover.

The annual energy production of solar panels is 1000 MWh per (ha year).[33] This value was used for the production of the three energy forms: electricity, HT heat and LT heat.

3 Results

3.1 Selected production routes

To evaluate potential routes for fossil-free routes for methanol and ethanol production, a wide variety of processes was identified (see Table 1). More detailed process information can be found in Appendix B.† Conventional routes were used as a benchmark. For this we selected natural gas-based production of methanol and sugar cane-based production of ethanol. Table 1 provides an overview of various production technologies for methanol and ethanol, focusing on reaction formula and short process description.

Based on our literature analysis we expect the alternative routes to mature within 25 years. Therefore, the prospected process and cost development for the novel technologies (*e.g.* DAC, hydrolysis, and co-electrolysis) are taken into account. An overview of energy consumption and CAPEX for the current and prospected 2050 scenario is shown in Table 2.

The CAPEX for a liquid-DAC system is currently 1060 M€ (corrected for CEPCI) to capture 0.98 Mton CO_2 per year, resulting in a CAPEX of 1080 € per (ton CO_2 per year).[36] This process requires a high-temperature energy demand of 0.36 MWh per ton CO_2 and electricity consumption of 1.5 MWh per ton CO_2.[37] In 2050, it is assumed that the complete system is electrified, as this would be a more sustainable alternative compared to using natural gas for supplying high temperature heat.[38] The CAPEX is expected to decrease to 290 € per (ton CO_2 per year) (corrected for CEPCI) with an electricity consumption of 1.3 MWh per ton CO_2 in this electrified high-temperature

Table 1 Overview of processes that were used to evaluate different methanol and ethanol production routes

Technology	Reaction formula	Description
Steam reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	Converts natural gas to syngas at 500–720 °C and[7] 29 bar
Anaerobic digestion	$(C_6H_{12}O_6)_n \rightarrow 3nCH_4 + 3nCO_2$	Converts energy crops and residues into biogas consisting of 50% CH_4 and 50% CO_2
Direct air capture (DAC)	CO_2 (in air) $\rightarrow$ CO_2 (captured)	Extracts CO_2 from the air with high-temperature and electricity demand
Hydrolysis	$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6$ $(C_5H_8O_4)_n + nH_2O \rightarrow nC_5H_{10}O_5$	Thermo-chemical and enzymatic process converting cellulose to glucose and hemi-cellulose to xylose
Co-electrolysis	$CO_2 + H_2O \rightarrow CO + H_2 + O_2$	Electrochemical conversion of CO_2 and water to syngas using high temperatures around[34] 850 °C
H_2O electrolysis	$2H_2O \rightarrow 2H_2 + O_2$	Splits water into H_2 and O_2 using a PEM electrolyzer
Dry reforming	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	Converts biogas to syngas at 1000 °C and 4.1 bar
Methanol synthesis	$CO + 2H_2 \rightarrow CH_3OH$	Process that convert hydrogen-enriched syngas to methanol[35] at 250 °C and 80 bar
1st generation fermentation	$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$	Microbial fermentation of glucose to ethanol and CO_2
2nd generation fermentation	$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ $3C_5H_{10}O_5 \rightarrow 5C_2H_5OH + 5CO_2$	Fermentation of hydrolysate (glucose and xylose) from corn stover to ethanol
Syngas fermentation	$2\ CO + 4H_2 \rightarrow C_2H_5OH + H_2O$	Microbial conversion of hydrogen-enriched syngas to ethanol
CO_2 fermentation	$3.8\ CO_2 + 9.6H_2 \rightarrow C_2H_5OH + 0.9C_2H_4O_2 + 4.8H_2O$	Fermentation of CO_2 and H_2 to ethanol and acetate
Ethanol dehydration	$C_2H_5OH \rightarrow C_2H_4 + H_2O$	Conversion of ethanol to ethylene

Table 2 Prospected development on energy consumption and CAPEX for direct air capture, H_2O-electrolysis and co-electrolysis

		Current	2050
CO_2 capture	Heat	0.36 MWh per ton CO_2	N.A.
	Electricity	1.5 MWh per ton CO_2	1.3 MWh per ton CO_2
	CAPEX	1080 € per (ton CO_2 per year)	290 € per (ton CO_2 per year)
H_2O electrolysis	Electricity	55 kWh per kg H_2	45 kWh per kg H_2
	CAPEX	1300 € per kW	320 € per kW
Co-electrolysis	Electricity	6.4 kWh per kg syngas	5.5 kWh per kg syngas
	CAPEX	6500 € per kW	650 € per kW

liquid DAC system.[38] These adjustments lead to a decrease in CO_2 capture costs from 400 € per ton CO_2 to 190 € per ton CO_2.

H_2O electrolysis splits water into hydrogen gas (H_2) and oxygen (O_2) using a Polymer Electrolyte Membrane (PEM) electrolyser. PEM electrolysers currently have an energy efficiency of 70%.[39] The reaction energy for splitting water is 39 kWh per kg H_2. Using this electrolyser efficiency and reaction energy, the energy requirement for H_2O-electrolysis was calculated to be 55 kWh per kg H_2. This corresponds to the electrical energy requirement of H_2O electrolysis that was modelled in SuperPro Designer[40] and to the values provided in the report of the Internation Renewable Energy Agency.[41] The PEC of a PEM electrolyzer for water electrolysis is currently 494 € per kW (corrected for CEPCI), and the CAPEX of the entire electrolyzer system is 1300 € per kW.[41] This results in a Lang factor of 2.6. In 2050, the energy demand for water electrolysis is predicted to decrease to below 45 kWh per kg H_2,[41] which corresponds to a electrolyzer efficiency of about 90%. The PEC is expected to decrease below 123 € per kW,[41] resulting in total system costs of 320 € per kW when using the same Lang factor as the current scenario.

Co-electrolysis can be performed at high temperatures (using solid oxide electrolyzer cell (SOEC) electrodes) and could therefore reach high faradaic energy efficiencies. It has been developed in recent years, and is currently at TRL 5–6.[34] The Purchase Equipment Costs (PEC) for a SOEC electrolyzer is currently estimated to be >2470 € per kW.[41] Using the same Lang factor, ratio PEC and total CAPEX, as was used for the H_2O electrolysis system and correcting for CEPCI, the CAPEX of co-electrolysis is currently estimated to be 6500 € per kW. The

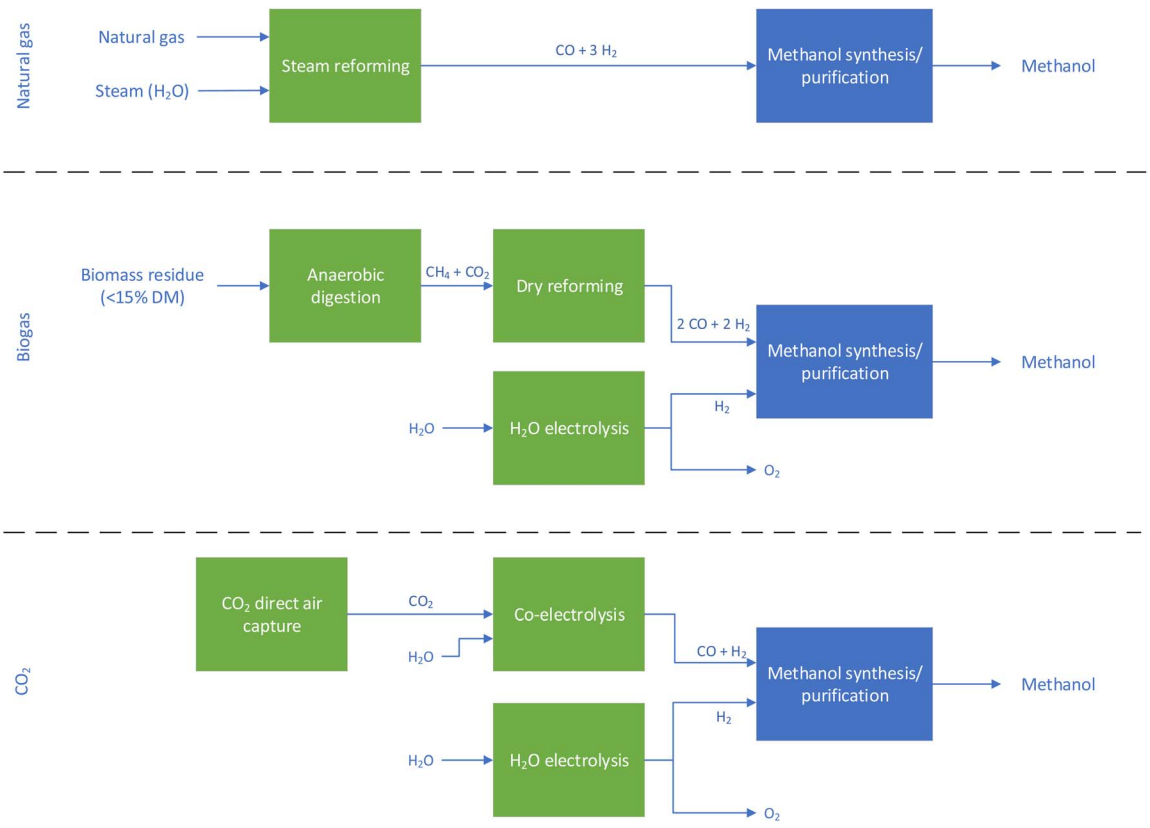

Fig. 1 Overview of evaluated methanol chemical production routes: the conventional route based on natural gas; a biogas-based route; and a CO_2-based route.

energy efficiency of SOEC electrolyzers is 82%.[39] Using this efficiency combined with the reaction energy of co-electrolysis (569 kJ mol^{-1}), the energy consumption of co-electrolysis is calculated as 6.4 MWh per ton syngas. In 2050, the PEC is expected to decrease to <247 € per kW, resulting in a CAPEX of the entire system of 650 € per kW. The energy efficiency is assumed to increase to 95% in 2050,[41] which will lead to an energy consumption of 5.5 MWh per ton syngas.

The proposed routes rely on organic carbon sources (*e.g.*, corn stover, maize silage, and cattle slurry) or CO_2 from liquid-direct air capture (DAC) or industrial point sources. We have purposefully selected a wide range of technologies where biomass-based approaches represent more mature technologies and CO_2-based approaches represent lower TRL technologies. We have also included DAC-derived CO_2 approaches, representing a high-cost scenario of 140–340 € per ton CO_2 as compared to CO_2 derived from point-source CO_2 at 30–60 € per ton from the literature.[42]

For methanol, three chemical production routes were evaluated. There are no fermentation processes to produce methanol: the conventional natural gas route, a biogas-based route using maize silage and cattle slurry, and a CO_2 route involving DAC and electrolytic syngas production (Fig. 1).

Ethanol production routes included conventional sugarcane fermentation, a second generation route based on lignocellulosic biomass hydrolysis, syngas from biogas fermentation, syngas from CO_2 fermentation and CO_2 fermentation using DAC-derived CO_2 and H_2 (Fig. 2). These routes represent varying levels of technical maturity and economic feasibility.

3.2 Methanol production

For a better understanding of each of the production routes, the techno-economic parameters of the processes of each route were evaluated first for methanol production. The results of the TEA for methanol production are shown in Fig. 3. The conventional natural gas route, with 0.4 k€ per ton methanol, is

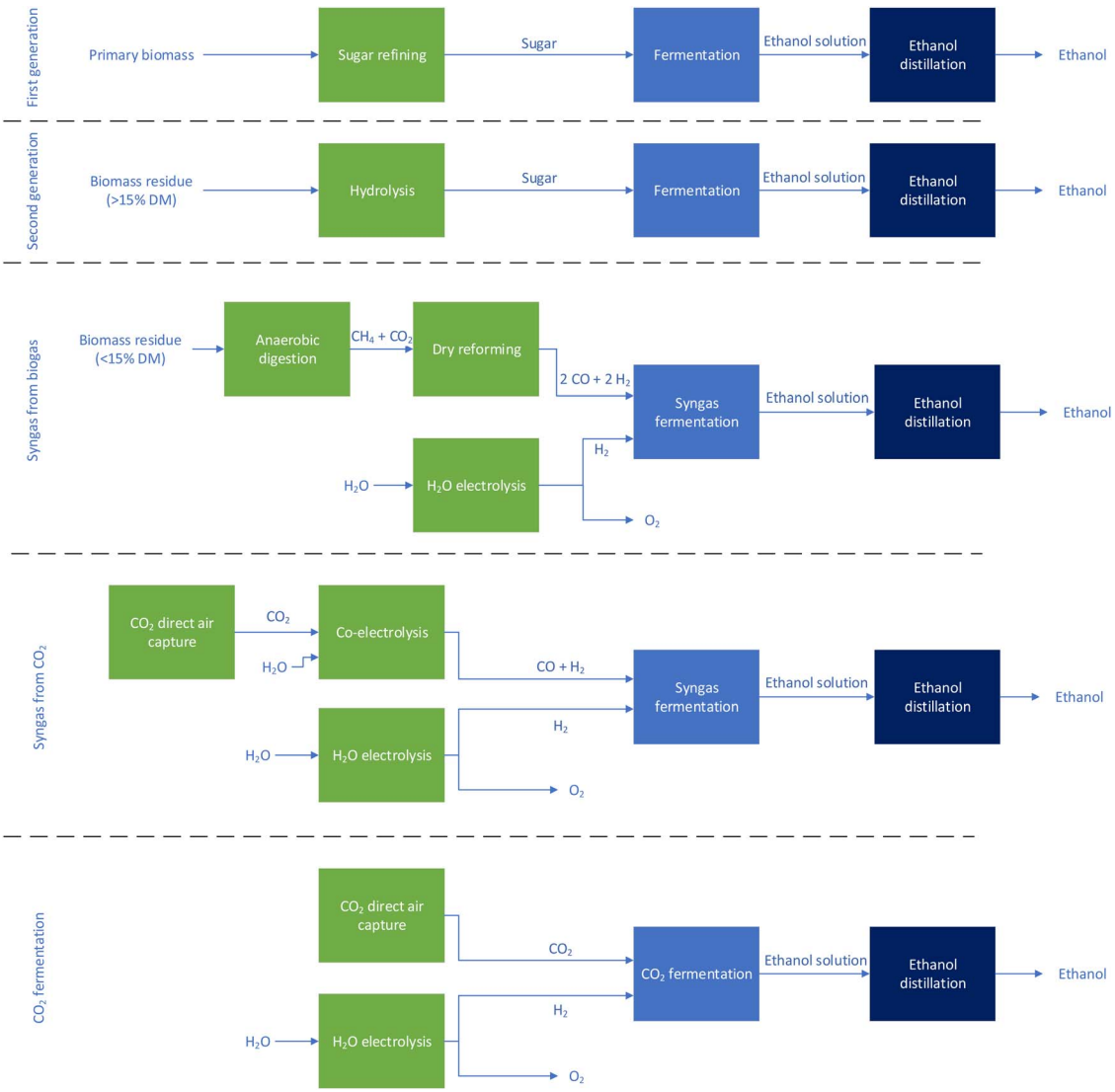

Fig. 2 Overview of evaluated ethanol fermentative production routes: the conventional route based on sugar cane; a second-generation based route, a biogas-based route, a syngas from CO_2 fermentation route, and a direct CO_2 fermentation route.

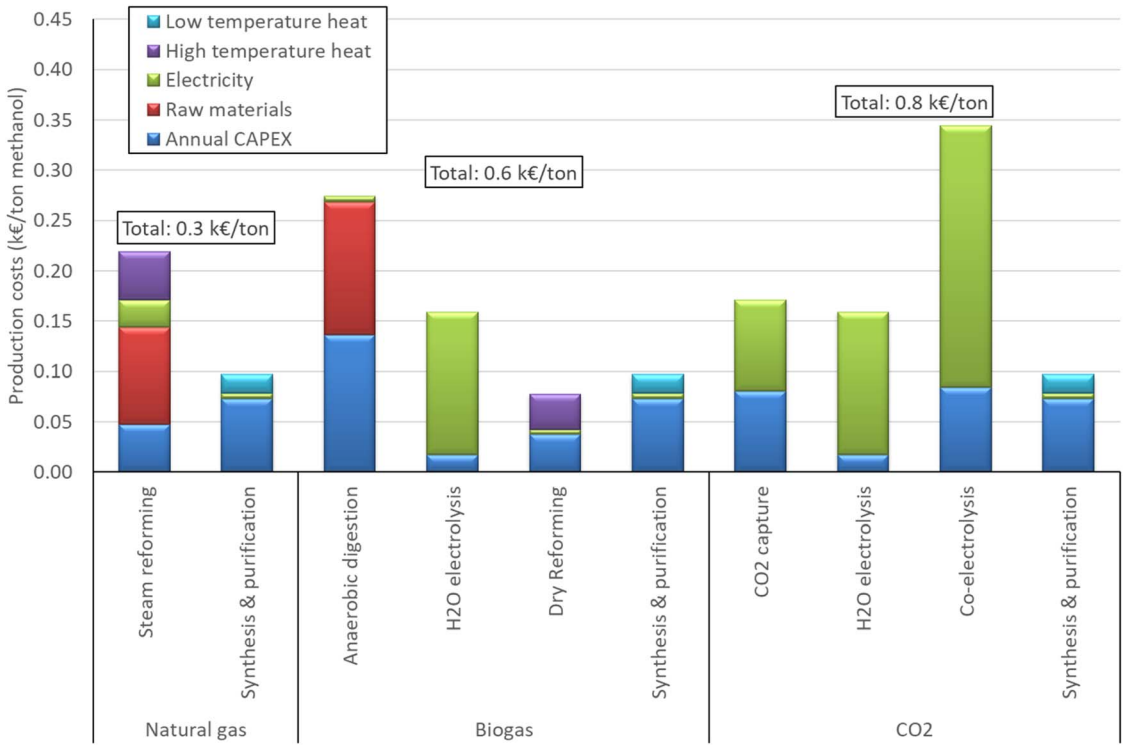

Fig. 3 Techno-economic assessment results of the evaluated methanol production routes. The production costs (€ per ton methanol) are the sum of annualized CAPEX, raw material, electricity, high temperature (HT) heat, low temperature (LT) heat and consumables.

the most cost-effective method to produce methanol. This estimated production cost corresponds to current market prices.[43–45] For conventional methanol production, annualized CAPEX, raw material (*i.e.* natural gas) and HT heat costs show the highest contribution. Even with the relatively low natural gas prices of the US, the raw material costs are roughly 100 € per ton methanol. It is important to note that when European natural gas prices of 40 € per MWh,[46] which is roughly 600 € per ton, are used, the raw material costs triple to roughly 300 € per ton methanol.

Our analysis of biogas conversion to methanol showed that the annualized CAPEX and raw material costs of the anaerobic digester (AD) represent 44% to the total costs. High annualized CAPEX costs are in part due to the small AD production scale. Additionally, the raw material costs represent 22% of total costs. These costs are a result of the input of maize silage required for the co-digestion. Finally, electricity for water electrolysis represents the highest cost factor for this route at 23%. It should be mentioned that these costs are highly dependent on the electricity prices assumed for the calculation (here 50 € per MWh).

The electricity costs dominate the production costs of the CO_2 route representing 65% of total costs. In this route, a significant amount of electricity is required to capture CO_2 from ambient air, and to convert it subsequently to syngas. Methanol synthesis and purification are similar for all routes. This is a well-developed large scale chemical production route, therefore showing relatively low annualized CAPEX and production costs. Since the electricity requirement of the alternative routes is high (Fig. 4), the electricity price has a large impact on the electricity costs for the alternative routes. Therefore, a scenario analysis on electricity prices is provided in Section 4.2.

Given that the energy costs showed wide variation, we made an overview of the total energy requirement for each route (see Fig. 4). This is set off against the heat of combustion of methanol (dashed line, Fig. 4). The energy requirement for the conventional route is the lowest with the biogas route requiring 188% more energy input. Using CO_2 as input for methanol formation requires extensive energy input. This is in line with expectations, as the energy contained in natural gas allows for low energy input conversion to syngas by steam reforming. When biogas is used as input, additional H_2 is needed for methanol synthesis, leading to additional energy requirement. Utilizing CO_2 as a raw material requires significant additional energy input because the chemical process demands energy to convert a low-energy molecule into a high-energy molecule. As the prospected development of the novel processes (DAC, H_2O-electrolysis and co-electrolysis) is already taken into account, it is expected that there is little room for further improvement on energy consumption and costs for these processes.

The conventional natural gas route is the most attractive route in terms of costs and energy efficiency. However, this route is based on fossil feedstocks, with a CO_2 emission of 2 ton CO_2 per ton methanol.[47] The non-fossil routes will not lead to net CO_2 emissions (Fig. 5).

When comparing the various non-fossil routes for methanol production, it is clear that with respect to energy requirement and costs, the use of biogas as a source for methanol synthesis

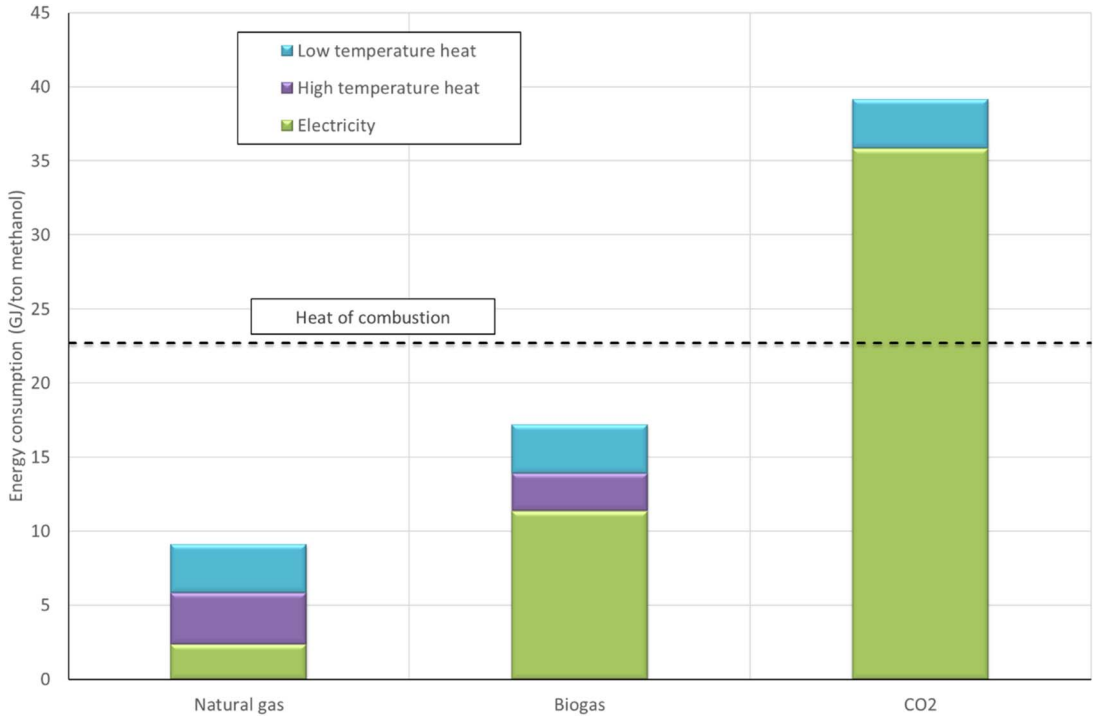

Fig. 4 Energy efficiency (GJ per ton methanol) of the evaluated methanol production routes. The total required energy is the sum of electricity and heat (low and high temperature). The total energy is compared to the heat of combustion of methanol to indicate the energy requirements.

may be preferred over the use of CO_2 directly (see Fig. 5). Given the high energy costs of both non-fossil routes, we also performed a sensitivity analysis using electricity and HT heat prices of 25 € per MWh, 50 € per MWh and 100 € per MWh indicated with error bars in Fig. 5, with LT heat prices set at 40% of HT heat prices. This shows that costs for the CO_2 route reach parity

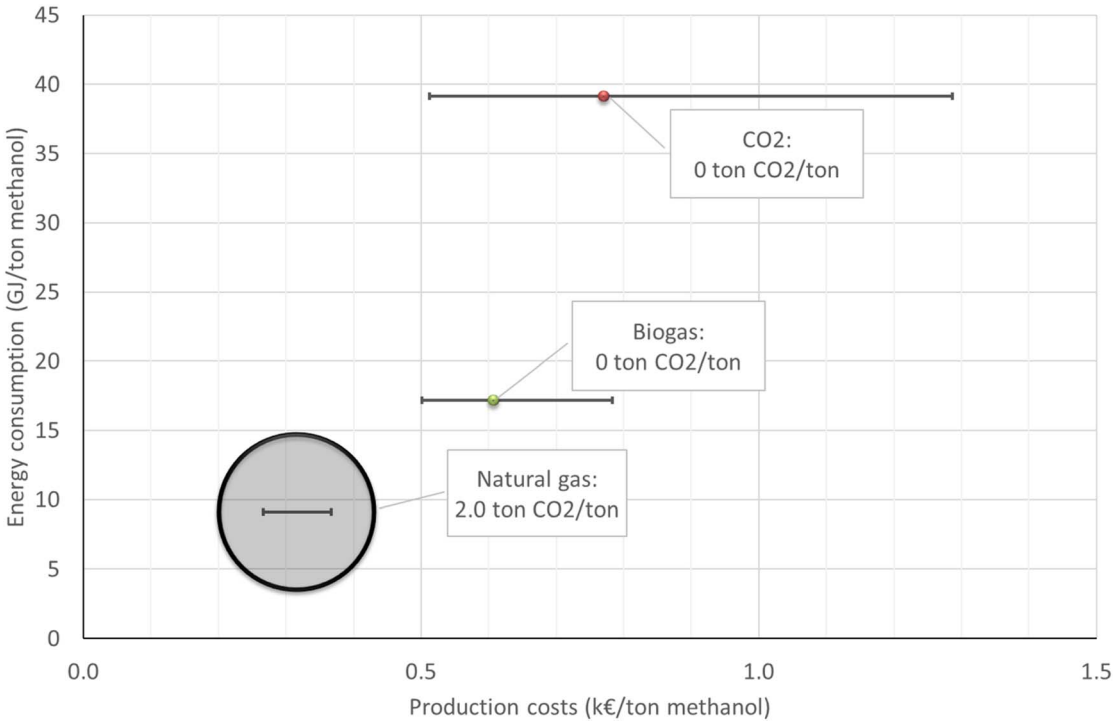

Fig. 5 Overview of production costs (x-axis), energy consumption (y-axis) and CO_2 emission (bubble size, also indicated in text) of the evaluated methanol production routes at 50 € per MWh. The error bars show the possible production costs at 25 € per MWh and 100 € per MWh for each production route.

with using biogas as an input for methanol formation at 25 € per MWh. Yet the energy requirements remain more than 2-fold higher.

3.3 Ethanol production

To expand on the understanding of using various production routes for chemical platform molecules, the techno-economic parameters for ethanol production were also assessed. Five different routes were studied, ranging from first-generation ethanol fermentation to CO_2 fermentation (Fig. 2). The results of the TEA of ethanol production are shown in Fig. 6. Using a first-generation biofuel process is the most cost-effective production method, according to our calculations, in line with expectations. The estimated production costs of 0.6 k€ per ton ethanol correspond to current market prices.[48,49] For the first- and second-generation routes, raw material costs are a large cost factor. The corn stover costs in the secondary fermentation route are even higher than the sugar cane costs in the first-generation fermentation route. Sugar cane is grown at low costs in Brazil, while corn stover is relatively expensive, as it has significant value in feed and material applications such as bedding and insulation. Interestingly, our calculations show that using either biogas or CO_2 as input and converting that to syngas *via* dry-reforming or co-electrolysis, respectively, results in similar overall costs as 2nd generation production of bio-ethanol. Using CO_2 as a direct input in CO_2/H_2 fermentation leads to high costs, mainly due to high energy and CAPEX requirements. The latter is mostly caused by the slow rates of the fermentations, leading to high investments in bioreactor facilities.

In the two routes that use CO_2 as input, it should be noted that the high electricity consumption is mainly caused by the Direct Air Capture (DAC) and electrolysis processes. Furthermore, the three routes that use biogas and CO_2 as input show relatively high fermentation & distillation costs compared to the first- and second-generation routes. These routes tend to be better developed and allow for reaching higher ethanol titres than the other 3 routes. This results in a marked difference in energy requirements for distillation. In Section 4.2, a scenario analysis on the electricity prices is provided.

Given the wide variation in energy costs, we compiled an overview of the total energy requirements for each production route, as illustrated in Fig. 7. These values are compared against the heat of combustion of ethanol (dashed line, Fig. 7). The energy analysis indicates that biomass-based routes generally require less energy input, as a substantial portion of the energy in the final product originates from the biomass itself. Notably, the first-generation fermentation route demonstrates a negative energy requirement, as it co-generates biomass residues that can be used to produce surplus electricity. In contrast, routes that capture carbon as CO_2 from the atmosphere demand substantial energy inputs, particularly for the production of syngas and subsequently ethanol.

Due to limited land availability, global bioethanol production using 1st and 2nd generation processes will not be able to supply all required bioethanol.[50] Therefore, all selected routes were subjected to a full trade-off assessment of the production

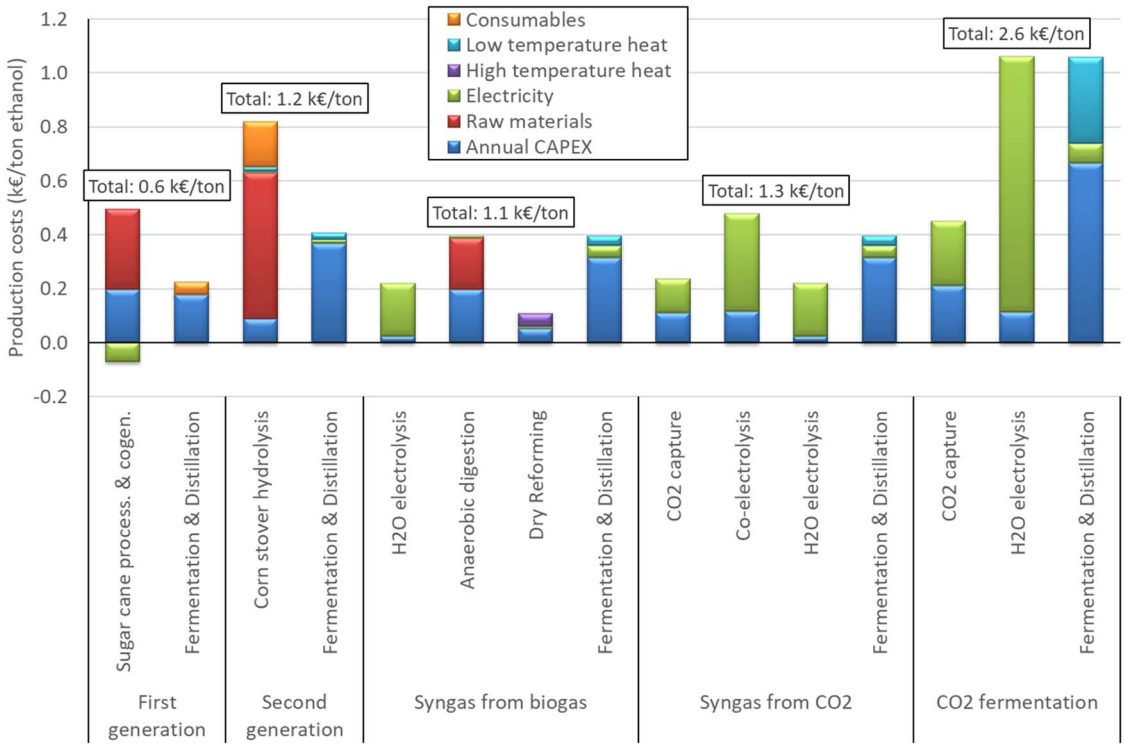

Fig. 6 Techno-economic assessment results of the evaluated ethanol production routes. The production costs (€ per ton ethanol) are the sum of annualized CAPEX, raw materials, electricity, heat (low temperature), heat (high temperature) and consumables.

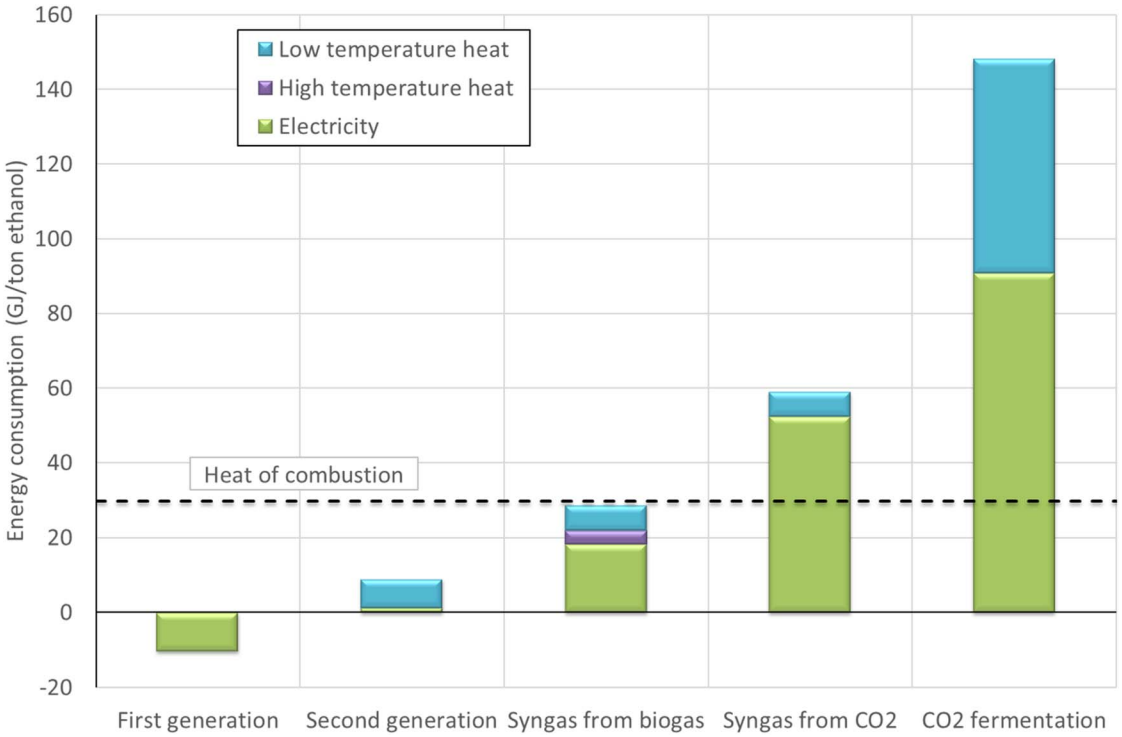

Fig. 7 Energy efficiency (GJ per ton ethanol) of the evaluated ethanol production routes. The total required energy is the sum of electricity and heat (low and high temperature). The total energy is compared to the heat of combustion of ethanol to indicate the energy efficiency.

costs, energy and land-use requirements of all the technologies (see Fig. 8). Given the high impact of the energy consumption on the overall costs, we performed a sensitivity analysis using energy prices of 25 € per MWh, 50 € per MWh and 100 € per MWh. Land use was normalized by estimating the required amount of solar panel area to generate the required electrical energy.

The 1st and 2nd generation routes lead to the largest land use, 0.20 and 0.19 ha year per ton ethanol, respectively. Required land use for the syngas from biogas route is smaller, as the electricity consumption is limited and the biomass used as input for biogas formation is based on a mixture of maize silage (10% FW) and cattle slurry (90% FW). Both CO_2-based routes require the least land use, as the land use is only based on solar panel area for electricity production.

The required areas of the alternative routes seem relatively small, especially when compared to the required area to grow biomass. However, these still represent significant areas required for the generation of renewable electricity, with corresponding investments in infrastructure that are required to produce ethanol *via* these routes.[1]

4 Discussion

4.1 Not included processes

In this paper, a large variety of biomethanol and bioethanol production routes was explored. Needless to say, not all potential conversion routes were analysed. The alternative processes that we have identified and have not included in this study are biomass gasification, reverse water gas shift reaction (RWGS), Fischer–Tropsch, and direct electrolysis of CO_2 to products (*e.g.* methanol). The reasons for not including these are discussed below.

Biomass gasification tends to lead to impure syngas mixtures, and therefore a purification step is required to remove *e.g.* H_2S and HCN. Additionally, we expect the energy efficiency to be low compared to other technologies that treat biomass for syngas production, such as anaerobic digestion, as high temperatures are needed.[51,52] Therefore, this process was excluded from our study.

Co-electrolysis was studied in this paper to investigate whether it would be a feasible technology to convert CO_2 into syngas. An alternative process would be the reverse water-gas shift reaction (RWGS, $CO_2 + H_2 \leftrightarrow CO + H_2O$). For RWGS, extra H_2 is required, which should be produced using water electrolysis. Since the efficiency of co-electrolysis is higher than that of water electrolysis, co-electrolysis was evaluated in this study.

Fischer–Tropsch is widely used in the petrochemical industry. Syngas is used as a feedstock to produce alkanes (C_6–C_8–C_{10}) and waxes. A (hydro)cracker is subsequently needed to break down larger alkanes. As this process produces a wide range of alkanes, and thus no methanol/ethanol, this process is out of scope for this study.

Direct electrolysis of CO_2 to methanol is an interesting upcoming technology to convert CO_2 directly to methanol in an electrolyser.[19,53] However, little process information was available in the literature, and the TRL of this process is currently considered too low for this study.

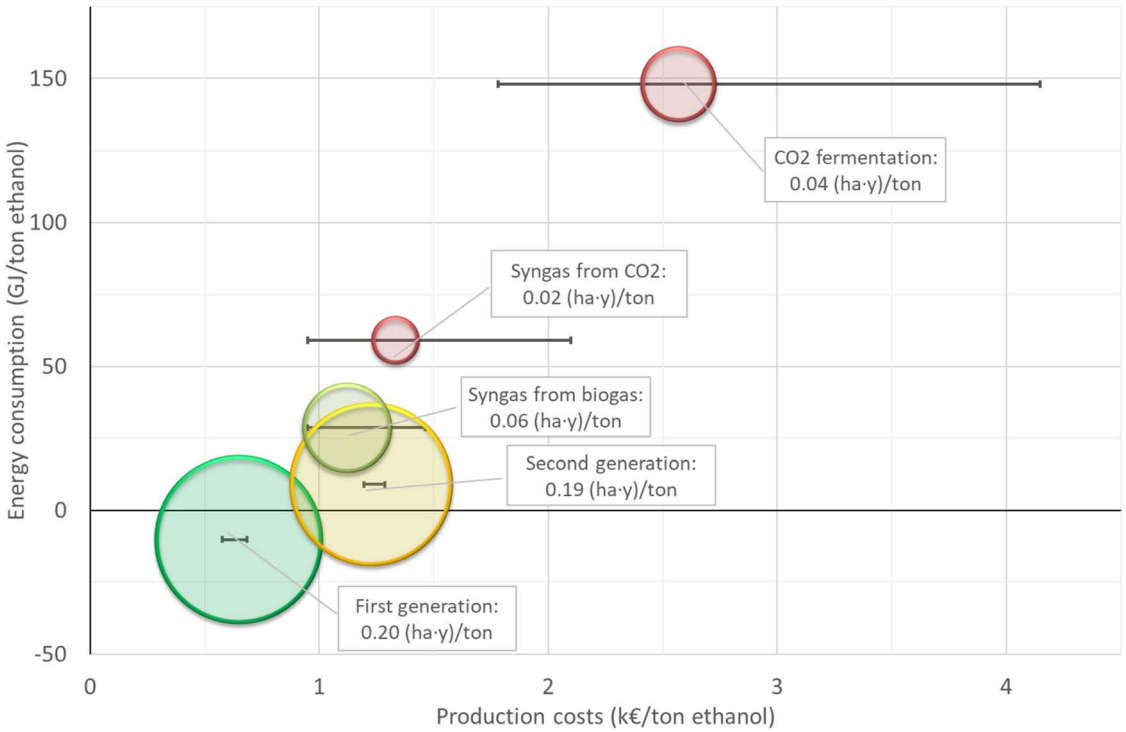

Fig. 8 Overview of land use, energy requirement and costs of the evaluated ethanol production routes. Land use ((ha year) per ton ethanol) is indicated by bubble size. Green indicates land use for growing crops. Orange indicates land use for growing crops and solar panels. Red indicates land use for solar panels. The land use of the first-generation route is corrected for the generated electricity (0.003 ha year per ton).

Finally, the routes that are evaluated in this study could be integrated, *e.g.* by using methane from biogas as input for steam reforming in the conventional route, or by using the CO_2 that is released during conventional first-generation fermentation as input for syngas fermentation.[20] When this CO_2 is upgraded to ethanol, the overall ethanol yield can be improved by 45%.[20] Using current state-of-the-art technology process values, however, the increased ethanol yield did not compensate for the higher costs, resulting in higher ethanol costs than the base-case. An increase in energy efficiency of electrolysers and in CO_2 electrolysis conversion efficiency, and a decrease in electricity costs would be needed to become cost competitive. As this was already reported elsewhere,[20] we did not include this in the current study.

4.2 Scenario analysis

Our TEA approach uses current prices for raw materials and energy. We also did not include CO_2 from point sources or CO_2 taxes. These TEA results show that alternative production routes are not yet cost-competitive with either the fossil-based methanol or 1st generation biobased ethanol production routes. Below, we discuss opportunities to reduce the costs of the alternative production routes to reach cost parity.

4.2.1 DAC *vs.* point-sources. This study assumes that CO_2 is obtained *via* DAC for the data shown in the Results section. In the CO_2-based routes, the electricity costs contribute significantly to the overall costs, mainly due to DAC and H_2O electrolysis and co-electrolysis. These electricity costs are linked to obtaining CO_2 from (diluted) air and converting the energy-poor CO_2 into energy-rich syngas, which is also concluded by Volta-Chem for similar processes.[54] The use of CO_2 from point sources instead of DAC will result in a strong decrease in CAPEX and electricity costs. The costs of CO_2 from point sources would be 60 € per ton,[42] instead of the calculated 124 € per ton CO_2 from DAC. We therefore assumed the use of point sources for the entire Section 4.2.

4.2.2 Electricity. It is unclear to what extent electricity may become cheaper in the future (the lowest electricity prices for solar energy are below 20 € per MWh). The expectation is that over the next few decades, the amount of renewable electricity will increase, and therefore, the costs will decrease.[28,55] We calculated the electricity price that would allow reaching cost parity with the current production routes for methanol and ethanol production. The CO_2-based methanol production route achieves cost parity, provided electricity prices are 6.0 € per MWh. Low electricity prices are insufficient to reach cost parity in the biogas route. For ethanol production, the electrolysis-syngas route achieves cost parity at 5.3 € per MWh. The other alternative ethanol routes will not achieve this. It should be mentioned that it is unlikely that electricity prices will reach such low prices. Low electricity prices can largely contribute to reducing costs, but alone they are insufficient to move away from conventional production routes.

4.2.3 CO_2 tax. Additionally, we did not include a CO_2 tax in the above calculations, given the challenges in predicting the carbon tax in 2050. It may be important to note that the French

Table 3 Cost parity for the different production routes based on CO_2 taxes in comparison to the fossil-based conventional route for methanol and ethanol production. In the alternative routes, CO_2 is obtained from point sources at 60 € per ton CO_2, and electricity costs are set at 50 € per MWh. An elaborate description of the routes is found in Fig. 1 and 2

Product	Route	Required CO_2 tax for cost parity to fossil route at 25 € per MWh (€ per ton CO_2)	Required CO_2 tax for cost parity to fossil route at 50 € per MWh (€ per ton CO_2)	Required CO_2 tax for cost parity to fossil route at 100 € per MWh (€ per ton CO_2)
Methanol	Biogas	117	145	200
	CO_2	101	182	344
Ethylene	First generation	268	268	269
	Second generation	841	915	1062
	Syngas from biogas	566	797	1259
	Syngas from CO_2	498	896	1692
	CO_2 fermentation	1367	2155	3733

government estimates that the CO_2 tax will be 750 € per ton CO_2, while Germany estimates 730 € per ton CO_2.[56,57] The current carbon tax in Europe is 74 € per ton CO_2.[58] Required carbon taxes were calculated for the alternative routes.

When we analyse the required carbon tax to reach cost parity with current fossil-based methanol production routes, based on biogas and CO_2 from point sources, we observe that in the lowest energy price scenario of 25 € per MWh, the required carbon tax is 117 and 101 € per ton CO_2, respectively (see Table 3). We think it is likely that such prices will be reached before 2050. Higher electricity prices result in higher carbon price requirements, yet these are all lower than the expected carbon price indicated above.

For bioethanol production, we were unable to make a comparison to a fossil-based source, and therefore, we recalculated the carbon price requirement for bioethylene production, which includes one additional dehydration step after bioethanol production. Information on OPEX, CAPEX and input for mass balances for the dehydration of ethanol to ethylene was obtained from the literature. Detailed information can be found in Appendices A and B.† During dehydration, 1.7 kg of ethanol is needed to produce 1 kg of ethylene.[59] Ethylene bulk prices are about 676–930 € per ton ethylene (735–1011 USD per MT).[60] For this assessment, world average prices over the past 3 years (2021–2023) of 907 € per ton ethylene were used.[61] The carbon footprint of ethylene is 1.56 ton CO_2 per ton ethylene.[62] Table 3 shows the required CO_2 tax to reach cost parity with fossil-based ethylene. First generation bioethylene production would become cost competitive with fossil-based bioethylene production at around 270 € per ton CO_2 (Table 3). Other scenarios require significantly higher carbon taxes. Production of bioethylene using either biogas or CO_2 results in minimal carbon tax requirements of 566 € and 498 € per ton CO_2, respectively (Table 3).

4.3 Reflection on raw material prices

Fossil routes will become more costly when raw material prices, *i.e.* natural gas, increase. Alternative routes will become more attractive. Current natural gas prices vary from around 200 € per ton in Henry's Hub in America to 600 € per ton in Europe.[23,46] When the natural gas prices increase to 490 € per ton, the current European CO_2 tax of 74 € per ton CO_2 is already sufficient to reach cost parity for methanol production from biogas, assuming no increase in biogas prices. For the CO_2-based route, gas prices need to increase to 650 € per ton with a CO_2 tax of 74 € per ton CO_2. This suggests that the European business case by itself could work. However, the cheap import of fossil-based methanol will make it difficult in practice.

In contrast, the alternative routes that use corn stover or AD feedstock mixture (maize silage and cattle slurry) can benefit from lower raw material prices. However, even without costs for these raw materials, the alternative routes will not be cheaper than the conventional methanol and ethanol routes.

4.4 Reflection on energy and land use

Finally, for alternative ethanol/ethylene production, there is a trade-off between costs, electricity input, and land use, which should also be taken into account (Fig. 8). The first-generation bioethylene production process requires an estimated 830 Mton sugar to produce the 230 Mton ethylene produced in 2022.[63] The current total yearly global sugar production is around 180 Mton,[64] requiring a very strong increase in total sugar production, which would impact land-use requirements (also see Fig. 8). This can be mitigated by recycling products/materials. When more products are recycled, less virgin material is needed, and hence, less land use is needed for the production of ethylene.

Similarly, the energy requirements of producing bioethylene from biogas or syngas are 59 GJ per ton and 112 GJ per ton, respectively, resulting in approximately 3600 and 7000 TWh of electricity requirements, respectively. This represents roughly 13% and 24% of total global electricity production in 2023.[65] In general, a significant increase in electricity production is required if such technologies use renewable energy instead of fossil oil.

4.5 Bottlenecks for alternative routes

The main bottleneck for the CO_2-based methanol production route is the large electricity requirements for DAC, H_2O electrolysis and co-electrolysis. This is also the case, to a lesser

extent, for the biogas-based methanol route. As is shown in Section 4.2.3, these alternative routes can be enabled through combining CO_2 tax and lower energy prices. For the biogas-based methanol route, other bottlenecks are large raw material costs and CAPEX for AD. CAPEX may be reduced by increasing scale to profit from economies of scale.

For the alternative ethanol production routes (syngas from CO_2, CO_2 fermentation, and to a lesser extent syngas from biogas), large electricity requirements for DAC, H_2O electrolysis and co-electrolysis are again an important bottleneck. As explained in Section 3.2, there is little room for further improvement on energy consumption for these processes. The energy requirements for obtaining H_2 from water and CO_2 from air are disproportional to the revenues made from ethanol. Other more oxidized chemicals, such as methanol, that contain more oxygen per carbon atom will be easier to produce from CO_2. For the syngas from biogas ethanol production route, the second bottleneck is large raw material costs and CAPEX for AD, which can be reduced by increasing scale. A large cost item in the second-generation route is high raw material prices. Although a decrease in raw material prices could significantly reduce total costs, this alone is not enough to enable the second-generation route. For the gas fermentation routes, in general, an increase of fermentation efficiency from syngas or CO_2 will be necessary to enable the feasibility of these alternative routes.

5 Conclusion

The production processes show a trade-off between costs, energy efficiency, and CO_2 emissions or land use. Conventional routes for methanol and ethanol production show the lowest production costs using energy prices of 50 € per MWh and no CO_2 tax. The highest costs in the alternative methanol and ethanol routes are associated with the conversion of CO_2 to the more reactive, hydrogen enriched, syngas. CO_2-based routes require large amounts of renewable energy. However, there are ways to reduce production costs by lowering energy prices, obtaining CO_2 from point sources instead of DAC, and by implementing CO_2 taxes.

Assuming the use of a CO_2 point source and cheap electricity, cost parity with fossil-based routes is hard to achieve. A way to reach cost parity with fossil-based routes is the implementation of a carbon tax, starting from around 100 € per ton CO_2 for methanol and 270 € per ton CO_2 for ethylene production routes.

Difference in raw material pricing can also increase the feasibility of the alternative routes. Specifically, methanol production from biogas will become feasible at a natural gas price of 500 € per ton and a CO_2 tax of 74 € per ton. Methanol production from biogas is the most promising alternative route studied in this paper. The CO_2-based alternative is attractive at a combination of low electricity prices and the use of point sources.

The biogas alternative route is also the most promising for ethanol or ethylene production. And again, the CO_2-based alternative is attractive at a combination of low electricity prices and the use of point sources. The 1st and 2nd generation processes for bioethanol and bioethylene production are limited by the amount of available land to grow the biomass. Recycling remains an important development to tackle this problem.

The level of technology development is an important factor for the alternative routes to be implemented. In the end, there are multiple variables that influence the feasibility of the alternative routes. A combination of market price development and governmental measures can allow for cost parity.

Data availability

Two appendices are included, which provide the data used in the article. The numbers are given explicitly, and a persistent identifier is also added.

Author contributions

Marc Lanting: conceptualization, writing – original draft, methodology, data curation, software, visualization; Juliën Voogt: conceptualization, writing – original draft, methodology, data curation, software, visualization; Koen Meesters: conceptualization, methodology, data curation, software, writing – review and editing; Daan van Es: conceptualization, writing – review and editing; Martijn Bekker: conceptualization, writing – review and editing, funding acquisition, supervision; Marieke Bruins: writing – review and editing, supervision.

Conflicts of interest

None.

Acknowledgements

This research was funded by the Wageningen University & Research Knowledge Base Programme KB34 "Circular & Climate Neutral Society" (KB-34-003-011) that is supported by financing from the Dutch Ministry of Agriculture, Fisheries, Food Security and Nature.

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