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Research article

Implications in the production of defossilized methanol: A study on carbon sources



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ABSTRACT

The transition of the current fossil based chemical industry to a carbon-neutral industry can be done by the substitution of fossil carbon for defossilized carbon in the production of base chemicals. Methanol is one of the seven base chemicals, which could be used to produce other base chemicals (light olefins and aromatics). In this research, we evaluated the synthesis of methanol based on defossilized carbon sources (maize, waste biomass, direct air capture of CO2 (DAC), and CO2 from the cement industry) by considering carbon source availability, energy, water, and land demand. This evaluation was based on a carbon balance for each of the carbon sources. Our results show that maize, waste biomass, and CO_2 cement could supply 0.7, 2, 15 times the carbon demand for methanol respectively. Regarding the energy demand maize, waste biomass, DAC, and CO_2 from cement demand 25, 21, 48, and 45 $\frac{GJ}{ton_{MeOH}}$ separately. The demand for water is 5300, 220, 8, and 8 $\frac{m^3}{tor_{max}}$. And lastly, land demand was estimated to 1031, 36, 83, and 77 $\frac{m^2}{tor_{max}}$ per carbon source. The high-demanding-resource production of defossilized methanol is dependent on the availability of resources per location. Therefore, we analyzed the production of defossilized methanol in the Netherlands, Saudi Arabia, China, and the USA. China is the only country where CO_2 from the cement industry could provide all the demand of carbon. But as we envision society becoming carbon neutral, CO_2 from the cement industry would diminish in time, as a consequence, it would not be sufficient to supply the demand for carbon. DAC would be the only source able to provide the demand for defossilized carbon.

1. Introduction

The chemical sector is the largest industrial energy consumer and the third largest industry subsector in terms of direct CO_2 emissions (IEA, 2022). These emissions are from the production process itself or from the combustion of fossil fuels to power the synthesis process. Each type of chemical industry has a different ratio of CO_2 emission from the process and from burning fossil fuels. The further emission of CO_2 to the atmosphere accelerates the rise of the global temperature and as a result the global climate changes (Mousavi et al., 2023).

Base chemicals production emitted 935 Mtons of direct CO_2 emissions in 2022 (IEA, 2023). This represents 47% of the 2 Gton CO_2 (Gabrielli et al., 2023) emitted by the chemical industry. These emissions can be reduced if renewable and carbon-neutral raw materials substitute fossil fuels supporting the envisioned goal of reaching carbon neutrality by 2050.

Methanol is a key base chemical, that if produced in a renewable and carbon neutral manner, will allow us to partially defossilize

the chemical industry. It can be used as a raw material to produce ethylene and propylene (light olefins) (Brovko et al., 2022) and benzene, toluene, and mixed xylenes (aromatics) (Li et al., 2021). Light olefins and aromatics, also called "high value chemicals" or HVC, plus ammonia and methanol are the seven base chemicals from the chemical industry (IEA, 2018). The demand for methanol reached 98 Mtons (IRENA and INSTITUTE, 2021), for light olefins 311 $\frac{Mt}{year}$ (Chen et al., 2022), and for aromatics 110 $\frac{Mt}{year}$ (IEA, 2018).

Nowadays, methanol synthesis is done via steam methane reformation, where natural gas or coal undergoes a thermochemical treatment where the present carbon and hydrogen form other molecules with different ratios of carbon and hydrogen. The synthesis gas produced from steam methane reforming is also known as "syngas". Syngas is composed of CO, H₂, and CO₂ (Abubackar et al., 2019). These compounds react and form new species. The ratio of the compounds and as a consequence, the formed species is dependent on the raw material

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used to produce syngas and the thermochemical process applied to it. However, for the synthesis of methanol the required molar ratio $\frac{CO_2}{H_2}$ is 1 · 3

For each mol of CO_2 there must be three times more hydrogen moles. The following reactions (Eqs. (1) and (2) are the main equations in the synthesis of methanol.

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O(\Delta H^{25} \, ^{\circ}C = -50 \frac{kJ}{mol})$$
 (1)

$$CO + 2H_2 \longrightarrow CH_3OH(\Delta H^{25} \, ^{\circ}C = -91 \frac{kJ}{mol})$$
 (2)

Coal and natural gas are the most common fossil fuels used for syngas production and need to be replaced by defossilized carbon and hydrogen. We refer to defossilized carbon and hydrogen to carbonneutral and renewable carbon/hydrogen. Different options exist to obtain defossilized hydrogen such as the production of hydrogen from fossil fuels and capturing the emitted CO_2 and water electrolysis powered by renewable electricity. We will focus on the latest because it does not require additional treatment of emissions. For defossilized carbon, there are a few sources as biomass and captured CO_2 .

Energy biomass and waste biomass are two general types of biomass. An example of energy biomass is maize. This is an energy crop that is widely used for biogas production. It can be thought of as the benchmark for the use of biomass thanks to its high biomass yield and good conversion rate into methane (Jankowski et al., 2020; Gerin et al., 2008). Another type of biomass is the organic fraction of municipal solid waste, referred to as waste biomass (WB). This type of biomass usually ends up in landfills or in the open air and using it as a carbon source is a better option.

Captured CO_2 is another raw material besides biomass to produce defossilized methanol (Pérez-Fortes et al., 2016). We refer to captured CO_2 as CO_2 captured from the air or from a point source as the cement industry. Different methods are available to capture CO_2 . The main principles of the technologies to capture CO_2 include physical or chemical absorption, adsorption, and separation by membranes (Wilberforce et al., 2021). Depending on the principle, flue gasses or air come into contact with the capturing material and by the application of high pressure or temperature the captured CO_2 is realized (Heidari et al., 2021). The use of captured CO_2 as a raw material has two main benefits. The first is its use as raw material diminishing the use of fossil fuels and the second is the reduction of CO_2 concentration in the atmosphere. On the other hand, the use of captured CO_2 to produce methanol requires an external source of hydrogen, which implies an extra step in the production process.

In literature, the use of different carbon sources to substitute fossil carbon in the chemical industry has been evaluated. Kätelhön et al. (2019) assessed globally the potential of captured CO_2 use in the chemical industry. Specifically for methanol, Gabrielli et al. (2023) reviewed biomass and captured CO_2 as sources of carbon, Pérez-Fortes et al. (2016) and Rosental et al. (2020) focused on captured CO_2 as the source of carbon, Rumayor et al. (2022) analyzed different scenarios to produce methanol based on the CO_2 emissions from the cement industry, and Ghosh et al. (2019) analyzed the production of methanol from biomass via anaerobic digestion. To our knowledge, this is the first publication that compares in a normalized way different sources of defossilized carbon to produce methanol.

The objective of this research is to highlight the implications of selecting a defossilized carbon source in the production of methanol and methanol as raw material to produce High Valuable Chemicals. The manuscript is organized as follows: in Section 2, it is described the indicators to evaluate the processes for the production of methanol based on the different carbon sources, Section 3 shows the demand for each of the indicators based on the source of carbon, then these results are placed in perspective by looking into the production of defossilized methanol at different locations (the Netherlands, Saudi Arabia, China, and the USA), and lastly Section 4 discusses the implications of using each one of the carbon sources to produce defossilized methanol and defossilized methanol as a raw material.

2. Methodology

2.1. Carbon availability, energy, water, and land demand as sustainability indicators

The indicators we analyzed for the production of methanol based on different carbon sources are carbon availability, energy, water, and land demand to run the process.

The availability of the raw materials is specific for each one of them. For maize, it was based on the yearly output of dry biomass per ha. This fraction of maize is considered as a whole, but the fraction which is related to the yield of biogas is the volatile fraction. In the case of WB, the waste is generated yearly per capita. For CO_2 , regarding the capture of it from the air, it is considered widely available. For CO_2 from cement flue gasses, the availability is based on the average production of cement per year and the percentage of CO_2 in the flue gas.

Methanol synthesis process slightly differs when using each of these raw materials. Each of the analyzed carbon sources requires different treatment to be used in the production of methanol as well as hydrogen content. Energy demand was normalized to $\frac{GJ}{\mathrm{ton}_{MeOH}}$ and water demand

was normalized to $\frac{m^3 H_{2O}}{ton_{MeOH}}$. Land demand is considered for the growth of maize, for the setting of CO_2 captors, and to produce the energy for the different processes that the synthesis of defossilized methanol requires. The selected technology to power the process is PV panels. The panels collect solar irradiation and convert it to electricity, this is done at 15% efficiency (Dwivedi et al., 2020). We calculated the annual power production based on the conditions of each one of the countries. For example, in the case of the Netherlands, an irradiance of $3.9 \frac{GJ}{m^2*year}$ was received in 2020 (Laevens et al., 2021), considering the efficiency of PV panels and the solar irradiance, $0.60 \frac{GJ}{m^2}$ power is achieved. Therefore, the amount of energy required per carbon source was divided by the power achieved per location to calculate the land demand ($\frac{m^2}{ton_{MeOH}}$).

2.2. Analysis of maize as carbon source to produce methanol

Fig. 1 shows the steps considered in the production of defossilized methanol based on maize and waste biomass. We considered the same steps for both carbon sources because they have similar characteristics, specifically in terms of water content. High water content in biomass makes a biological approach preferable over thermochemical treatments due to the significantly lower energy demand required for the treatment.

Maize global production reached 1.1 Gton in the period 2017–2019 (Erenstein et al., 2022), resulting in 330 Mton of dry mass. The energy inputs associated with its production are shown in the Supplementary Material, table 1. The water demand for maize growth includes the surface and groundwater, as well as the rain water (Table 1). Once that maize has been harvested, the next step is the production of biogas.

The production of biogas is done via anaerobic digestion. We considered the conditions as in Gómez-Camacho et al. (2021), where the anaerobic digestion plant comprises pre-digestion treatment, digestion and co-generation, and post-digestion. The produced biogas in anaerobic digestion is a mix of CH_4 and CO_2 and traces of other elements such as N_2 , H_2S , O_2 , and H_2 (Kang et al., 2010).

In order to separate bio-methane and CO_2 , biogas is upgraded via water gas scrubber. Two streams will be obtained one for bio-methane and one of CO_2 . To use all the available carbon from maize, this CO_2 fraction will be circulated to the production of methanol.

The bio-methane fraction is reformed via steam reforming. This approach is considered the most thermodynamic suitable treatment of biogas for the synthesis of methanol (Vita et al., 2018). In the Supplementary Material section S2.2, we show in more detail the influence of

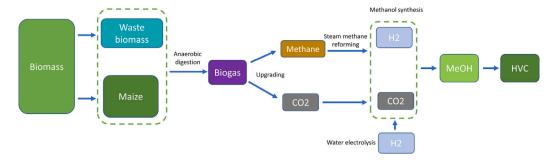


Fig. 1. Maize and waste biomass follow the same process in the production of defossilized methanol.

Table 1

Energy, water, and land demand for maize and WB as carbon source in the production of methanol.

Process	Energy demand	Water demand	Land demand
Maize growth	25 GJ a	$1028 \frac{m^3}{\text{ton maize}} f$	50 ton _{maiz} h ha
Anaerobic digestion (maize)	489 $\frac{\text{MJ}}{\text{ton}}^{b}$	$0.028 \frac{m_{\text{water}}^3 b}{\text{ton}_{\text{maize}}}$	
Anaerobic digestion (WB)	938 $\frac{\text{MJ}}{\text{ton}}^{b}$	$0.13 \frac{m_{\text{water}}^3 b}{\text{ton}_{\text{WB}}}$	
Biogas upgrading	$0.3 \frac{\text{kWh}}{\text{m}_{\text{biogas}}^3} c, d$	$0.27 \ \frac{\mathrm{m}^3}{\mathrm{m}_{\mathrm{biogas}}^3} g$	
Syngas production	$0.206 \frac{\text{MJ}}{\text{mol}_{\text{CH}_4}} i$	$0.1 \ \frac{\mathrm{m_{H_2O}^3}}{\mathrm{ton_{maize}}} i$	
Methanol synthesis	$0.56 \frac{\text{MJ}}{\text{kg}_{\text{MeOH}}} e$		

- ^a Jankowski et al. (2020) ^b Gómez-Camacho et al. (2021) ^c Collet et al. (2017) ^d Kapoor et al. (2019)
- ^e Eggemann et al. (2020) ^f Mekonnen and Hoekstra (2011) ^g Pacetti et al. (2015)
- ^h Murphy et al. (2011)
- * Based on the enthalpy of the reaction

the reforming on the total carbon efficiency and as a consequence the energy demand. The next process is the synthesis of methanol based on ${\rm CO_2}$ and ${\rm H_2}$. Where syngas, obtained from steam methane reforming, is previously conditioned to have a ratio 1 : 3 carbon to hydrogen before entering the synthesis reactor. Since the ${\rm CO_2}$ separated in the upgrading of biogas will be used, extra hydrogen is required. In Table 1, the energy, water, and land demands for each of the mentioned steps are included.

We calculated the carbon efficiencies from raw material to methanol. To assess the production of bio-methane and ${\rm CO}_2$, we considered the molecule of maize as: $({\rm C}_{3.5}{\rm H}_{6.2}{\rm O}_{2.99}{\rm N}_{0.04})$ (Biller et al., 2017) and applied the Buswell equation. In the Supplementary Material section S2 and S2.1, it is shown this calculation. The result of this carbon efficiency is the ratio of ton of maize per ton of methanol, which will be used to later calculate the availability of carbon sources based on the amount of carbon needed to supply the demand for carbon in the production of methanol and HVC. From the maize carbon balance, it is also estimated the amount of hydrogen needed. Hydrogen will be produced via water electrolysis. Calculations for energy and water demand are shown in the Supplementary Material section S3.

2.3. Analysis of waste biomass as carbon source to produce methanol

Municipal solid waste can be used for the production of biogas. This is preferred over thermochemical treatment since municipal solid waste has a low heating value (Panigrahi and Dubey, 2019) due to the high organic fraction present. Therefore, our focus lays on the harnessing of organic fraction of solid municipal waste, referred to as waste biomass (WB), to produce methanol via anaerobic digestion. By selecting this approach, it is also possible to compare WB to maize as sources of carbon to produce methanol, as shown in Fig. 1.

The production of methanol via WB follows the same route as the one from maize: anaerobic digestion, biogas upgrading, and methanol synthesis. The difference between the two biomasses is the elemental composition and the variety that WB could have based on where and in which season of the year is being produced. We considered the values

from Gómez-Camacho et al. (2021), where the anaerobic digestion of energy crops and the organic fraction of municipal solid waste were analyzed by looking into the energy demand of the process.

In Table 1, we show the practical values used for the calculation of energy, water, and land demand for maize and WB.

To calculate the carbon efficiency for WB, we considered the elemental composition of WB as $C_{32}H_{55}O_{16}N_1$ (Komilis et al., 2012). Then we followed the same carbon balance of maize. The amount of potential WB as raw material is calculated as the amount of municipal solid waste produced 2.01 $\frac{\text{Gion}_{\text{wastebiomass}}}{\text{year}}$ (Kaza et al., 2018), and 44% represents the organic fraction, the total potential available amount would reach 884 Mton of WB.

2.4. Analysis of CO₂ from the air as carbon source to produce methanol

 ${\rm CO}_2$ is available in the air at a concentration of 417 ppm (Administration, 2023) and can be captured directly from the air. This technology is referred to as direct air capture (DAC). Where ${\rm CO}_2$ is separated from the air to form a more ${\rm CO}_2$ concentrated stream. The most developed technologies to achieve this can be classified as liquid solvent and solid sorbent (McQueen et al., 2021). The difference in technologies relies on the material where ${\rm CO}_2$ will be captured. We will focus on liquid solvent because it can be used for DAC but also in the capture of ${\rm CO}_2$ in point sources.

Fig. 2 shows the steps in the use of captured CO_2 to produce defossilized methanol. First CO_2 is captured, either from the air or from the flue gasses from the cement industry, then hydrogen is produced via alkaline water electrolysis, and lastly methanol is produced. Methanol could be used directly or it could be used to produce high valuable chemicals.

The values considered for energy, water, and land demand are included in Table 2.

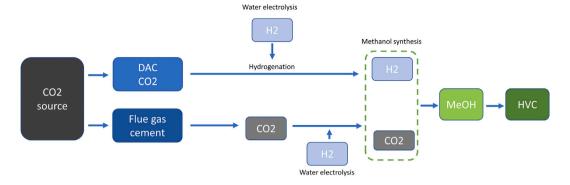


Fig. 2. The production of defossilized methanol from captured CO2 has three main steps: CO2 capture, hydrogen production, and methanol synthesis.

Table 2
Energy, water, and land demand for captured CO₂ in the production of methanol.

Process	Energy demand	Water demand	Land demand
CO ₂ air	8.8 $\frac{GJ}{ton_{CO_2}}a$	$4.7 \frac{\text{ton}_{\text{H}_2\text{O}}}{\text{ton}_{\text{CO}_2}} d$	$1.5 \frac{\text{km}^2}{\text{Mton}_{\text{CO}_2}} e$
${\rm CO_2}$ capture from cement	$7.08 \frac{\text{MJ}}{\text{kg}_{\text{CO}_2}}^{b}$	$0.528 \frac{kg}{kg_{CO_2}}^b$	
Hydrogen production	$188 \frac{GJ}{tonH_2}^c$	9 $\frac{\text{ton}_{\text{H2O}}}{\text{ton}_{\text{H}_2}}c$	

^a Custelcean (2022) ^b Voldsund et al. (2019) ^c Rihko-Struckmann et al. (2010)

2.5. Analysis of flue gasses from the cement industry as carbon source to produce methanol

 ${\rm CO}_2$ emissions in the production of cement come from the process it self and from the combustion of fossil fuels. Cement production is based on the oxidation of limestone (CaCO $_3$) to calcium oxide (CaO), in this oxidation ${\rm CO}_2$ is emitted representing around two-thirds of the total ${\rm CO}_2$ emissions from the cement production process (Voldsund et al., 2019). Generally, Portland cement has 60% of CaO which would yield 0.471 $\frac{{\rm tonCO}_2}{{\rm tonCement}}$ (Andrew, 2018). 4.3 Gtons of cement were produced globally in 2020, which results in 2 Gtons of ${\rm CO}_2$ emitted. Therefore, even if cement production is based on renewable and carbon neutral electricity ${\rm CO}_2$ emissions would be still present.

 CO_2 capture in the cement industry is done in the emitted flue gasses. These gasses can have $18\%~\mathrm{CO}_2$ mole fraction. Amine scrubbing is the most mature technology for the capture of CO_2 in the cement industry (Hills et al., 2016). The values to calculate the energy, water, and land demand for the capture of DAC CO_2 and the cement industry are shown in Table 2. The carbon efficiency for CO_2 from the cement industry and CO_2 captured from the air is based on the number of carbon moles needed for the production of methanol.

2.6. From methanol to light olefins and aromatics

We would like to put into perspective the use of methanol to produce of other base chemicals, light olefins (ethylene, propylene), and aromatics (benzene, toluene, and mixed xylenes). For the production of olefins from methanol, 2.39 kg per kg of olefins are needed (Dimian and Bildea, 2018). In the case of aromatics, this is 5 kg methanol per kg aromatics (Zhang et al., 2019). Based on the current demand for these chemicals, the demand for methanol for olefins would be 610 Mtons, but considering that 19% of methanol consumption is already being done to produce light olefins (Tabibian and Sharifzadeh, 2023), then the demand for methanol diminishes to 602 Mtons. For aromatics, 550 Mtons of methanol would be needed. Here we make the distinction between methanol and methanol for HVC production. The demand for methanol for HVC production would reach 1152 Mtons. The total demand for methanol would be 1250 Mtons.

2.7. Assumptions for the suitability of carbon source per location

To assess the suitability of a carbon source per location, we will compare the availability of resources to the demand of resources for each carbon source. The comparison will be based on the calculated demand of resources of the carbon sources and the available resources per country. To indicate the suitability of a carbon source with respect to the indicators, we will use four colors. Green would mean that there is enough of the resources demanded for a carbon source in a specific location. Yellow will indicate that there might not be enough of the carbon source to satisfy the demand of carbon for methanol and methanol to produce HVC, but it can contribute to the total demand. Orange will be used to indicate that the required resources are potentially available and the color red will be used when there is no resources available. Then based on these colors, the carbon sources will be ranked based on the availability of resources. In the case that the carbon sources have the same colors, then the ranking will be based in the lower energy demanding carbon source. If a carbon source has a red color in any of the indicators, then it will not be considered as suitable.

3. Results

3.1. Availability of carbon sources

Based on the carbon balances for each of the carbon sources, we estimated the following ratios of carbon source per ton of methanol: 4.9 $\frac{\text{ton}_{\text{maize}}}{\text{ton}_{\text{meoh}}}$ (this ratio would be in dry matter, which is the 34% of maize), 4.5 $\frac{\text{ton}_{\text{WB}}}{\text{ton}_{\text{meoh}}}$, and 1.3 $\frac{\text{ton}_{\text{CO}_2}}{\text{ton}_{\text{meoh}}}$. Considering these ratios and the production of the different carbon sources, we estimated (if we were to use all the produced carbon sources for methanol production) a ratio of the carbon source to the demand of methanol.

Fig. 3 shows this estimated ratio. For defossilized methanol production, waste biomass could supply two times the carbon demand. The challenge of waste biomass use is that its composition changes on location as well as the time of the year when it is available. And for the production of defossilized methanol for HVC production, it could provide 0.1 times the carbon demand.

^d Keith et al. (2018) ^e Fasihi et al. (2019)

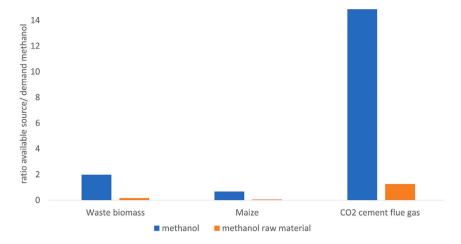


Fig. 3. Availability of carbon sources. Captured CO, is the only source available to supply the carbon demand for methanol and methanol to produce HVC.

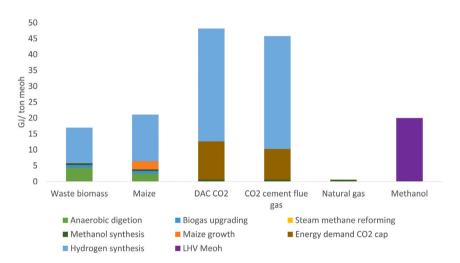


Fig. 4. Energy demand of the carbon sources. Captured CO2 is the carbon source that requires the most energy.

The use of maize for methanol production would require at least double the current production in order to supply enough carbon for methanol. For methanol for HVC production, it could supply 0.05 times the carbon demand. The cement industry could supply 15 times the carbon demand to produce methanol. Nevertheless, the location of cement factories would imply the production of defossilized methanol in the same regions. For example, the greatest cement production is in China, where 1.17 Gton CO2 were emitted in 2021. This CO2 could supply enough carbon for the production of 8 times the current demand for methanol. In this country, three quarters of methanol production are based on coal and the rest on natural gas (Yang and Jackson, 2012). The substitution of these fossil fuels for CO₂ from the cement industry is of great benefit to diminish CO₂ emissions. For methanol for HVC production, the global cement industry can provide one time the required carbon. DAC CO₂ is an infinite carbon source as long as there is available renewable energy. Therefore, assuming enough renewable energy we can also assume enough carbon for methanol and methanol for HVC production available.

3.2. Energy requirements to produce defossilized methanol

Fig. 4 shows the energy demand in GJ for the production of one ton of defossilized methanol. WB is the least energy demanding raw material and its energy demand is almost the same as the energy released when methanol is combusted. This low energy demand compared to

maize is that we assumed no energy demand in the production of WB since it is a waste. Maize follows WB as the least energy demanding carbon source, followed by CO2 from the cement industry and lastly, CO₂ from the air. Natural gas is also presented in the figure. Its energy demand is the lowest compared to the defossilized carbon sources. The difference in energy demand of biomass versus captured CO₂ is greatly influenced by the energy demand to capture CO₂ and the production of hydrogen. Hydrogen production represents the biggest energy demand for the production of methanol for all the proposed carbon sources. WB and maize are sources of carbon and hydrogen. Both have a similar ratio of 1: 1.7 carbon to hydrogen. Therefore, biomasses still need 1.3 times more hydrogen to reach the ideal ratio of 1: 3 to produce methanol. The difference in energy demand for the production of hydrogen among biomasses relies on the production of bio-methane. WB produced biogas with a concentration of 56% bio-methane while maize produced 50%. This difference is reflected in 21% higher energy demand for hydrogen synthesis. WB has a higher dry matter content than maize and based on the dry matter content we based the amount of available carbon. Furthermore, the CO₂ separated in the upgrading of biogas is used in the synthesis of methanol increasing the demand for hydrogen. Regarding the capture of CO2 as a carbon source, hydrogen production represents 72% of the total energy demand.

The energy demand to produce methanol from natural gas could reach 2 $\frac{GJ}{ton_{meoh}}$ (Chen et al., 2019; Li et al., 2018b). In our estimations based on carbon balance, the energy demand reaches $0.56 \frac{GJ}{ton_{meoh}}$, the

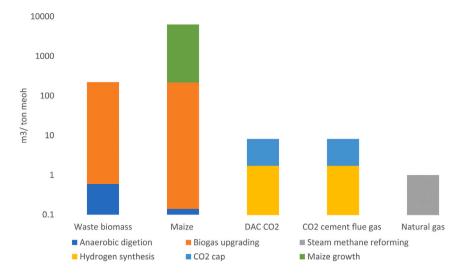


Fig. 5. The water demand of the different carbon sources. The graph has a logarithmic scale in the Y axis, where it can be seen that natural gas demands the least water compared to the analyzed carbon sources.

difference in the energy requirement relies that in the literature, a secondary reforming based on oxygen is considered. Therefore, more energy is needed for the air separation unit. Regarding the energy demands of the carbon sources, Rosental et al. (2020) studied the use of CO_2 from air and from point sources for the production of methanol and the energy demand calculated from DAC was $60 \, \frac{\text{GJ}}{\text{ton}_{\text{mech}}}$ and for point sources 45 $\frac{\text{GJ}}{\text{ton}_{\text{mech}}}$. Our results are in the same range and the difference in energy demands relies upon the consideration of a higher carbon demand of 1.44 $\frac{\text{CO}_2}{\text{MeOH}}$ vs. 1.37 $\frac{\text{CO}_2}{\text{MeOH}}$, a lower conversion of CO_2 to methanol 93%, and the addition of the energy demand for the infrastructure of CO_2 and hydrogen production.

3.3. Water requirements per ton of defossilized methanol

Fig. 5 shows the different water demands of the carbon sources. These water demands were also calculated by considering the ratio of carbon source to methanol and then the water demand of the carbon source for the different steps.

Maize is the most water demanding carbon source. Its grow demands 96% of the total demand. The value considered for maize growth is an indicator of the water footprint of maize production and considers the evaporation of water, soil/water balance, time of the year, as well as geographical location. Therefore, this value could change for specific locations and it could also be diminished by selecting locations with a high annual rainfall and having healthy soils that are able to retain water.

After water demand for the growth of maize, the most water consuming process for the analyzed biomasses is biogas upgrading. A less water demanding technology could have been chosen but water scrubbing is a mature technology and it is also possible to separate CO_2 from the water stream. For DAC CO_2 or CO_2 cement, the highest water demand is the capture of CO_2 . Water is required for the production of the solvent as well as for its regeneration due to evaporation. This loss is dependent on the ambient temperature. The higher the temperature, the higher the water loss.

Methanol production based on coal requires 9.03 $\frac{m_{H2O}^3}{ton_{meoh}}$ (Li et al., 2018b) to 20 (Li et al., 2018a), for natural gas the demand is around 14 $\frac{m_{H2O}^3}{ton_{meoh}}$ (Li et al., 2018b). The water demand for the production of methanol based on waste biomass is 11 times bigger than the water demand for the production of methanol based coal. For maize, this is even bigger by more than 300 times.

Comparing the water demand for the production of methanol and methanol for HVC production to the global renewable surface and groundwater (54700 km^3) (FAO, 2019) minus the global water consumption 4600 km^3 (Boretti and Rosa, 2019), it seems that there is enough water for the production of the chemicals. Nevertheless, the availability of water is not the same globally. So if these chemicals are produced based on either of these carbon sources, they need to be produced in a location where the availability of renewable water is greater that the current consumption.

3.4. Land requirement per ton defossilized methanol

The land demand has a similar behavior as the energy demand with exception of maize which almost reached the 1000 $\frac{m^2}{\tan_{mech}}$ (Fig. 6). Since WB requires the least energy demanding source, it will also require the least land area. Furthermore, for this carbon source land is only demanded for the production of energy. For DAC, it is also necessary land to capture CO_2 . The land demand for DAC contactors for CO_2 captured via liquid solvent reached 2 $\frac{m^2}{\tan_{mech}}$.

If the production of methanol (98 Mtons) would be based on these carbon sources the land demand would be; $3.5~{\rm km}^2$ for WB, $100~{\rm km}^2$ for maize, DAC CO $_2$ 8 km 2 , and $7.5~{\rm km}^2$ for CO $_2$ cement. Comparing these land demands to the size of a city, for example, Amsterdam which area is $41~{\rm km}^2$, for maize the land demand is more than 2 times the area of Amsterdam.

Land demand could be reduced if the production of electricity would be done in a high solar irradiating country such as Nigeria. The solar irradiation there can reach 9.18 $\frac{GJ}{m^2*year}$ (Abubakar Mas'ud et al., 2016). If the solar panels were located there, the land demand for energy production can be halved. Yet, the transportation of the generated electricity and the development of infrastructure are challenges to keep in mind.

For the production of methanol for HVC production, the land demand based on the source of carbon would be; waste biomass $43~\rm km^2$, maize $1231~\rm km^2$, DAC CO₂ $98~\rm km^2$, and CO₂ cement $92~\rm km^2$. Land demand is one magnitude bigger than the land demand for only the production of methanol.

3.5. Methanol and high-value chemical production based on location

The availability of a resource is bounded by location and influences the selection of a carbon source. In the previous section, we referred

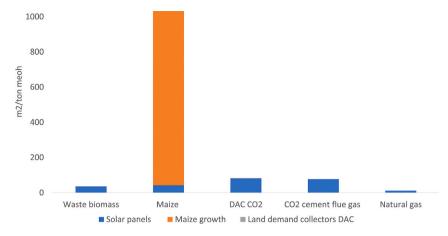


Fig. 6. Land demand of the analyzed carbon sources. Maize is the most land demanding carbon source.

Table 3
Resources per country. All the countries have the potential to produce enough energy to produce methanol and HVC. Water and land are more limited resources.

Indicator	Netherlands	Saudi Arabia	China	USA
Solar energy potential (EJ)	132 ^a	13 083 ^a	47 700 ^a	46 040 ^a
Solar energy (EJ)	0.033^{b}	0.002^{i}	0.090^{o}	0.053^{u}
Renewable water	91 ^c	2.4c	2840 ^c	3069 ^c
Resources (km ³)				
Water demand (km ³)	14.7 ^d	26^{j}	602^{p}	444 ^v
Land potential agriculture	No more land available ^e	No climate conditions ^k	Decrease of agricultural land ^q	Cropland expansion ^w
Carbon sources (mtons)				
Waste biomass	2.1^{f}	6 ¹	121 ^r	61 ^x
Maize (dry fraction)	2.8^{g}	0.5^{m}	86 ^s	114 ^y
CO ₂ cement	0.5^{h}	25 ⁿ	1100'	40 ^z

- ^a The World Bank (2020) ^b IRENA (2022c) ^c FAO (2019) ^d CBS (2021) ^e Quax et al. (2022) ^f De Leeuw and Koelemeijer (2022)
- 8 CBS (2022a) h Kemp et al. (2017) IRENA (2022a) Morsy and Othman (2021) Al-Nashwan et al. (2019) Rahman et al. (2022)
- ^m Al-Nashwan et al. (2019) ⁿ Wang et al. (2021) ^o IRENA (2022b) ^p Yangtze Institute for Conservation and Development (2021)
- ^q Fei et al. (2021) ^r Yang et al. (2021) ^s Liu et al. (2021) ^t Zhang et al. (2021b) ^u IRENA (2022d) ^v Ritchie and Roser (2018)
- ^w Lark et al. (2020) * EPA (2018) * U.S. Grains council (2019) * U.S. Geological Survey (2018)

to the global availability of carbon sources as well as the demand for methanol and methanol for HVC production. Yet, the availability of carbon sources and the production of methanol is done locally. Therefore, we selected four different countries to analyze the local production of methanol and methanol for HVC production based on the studied carbon sources. The selected countries are the Kingdom of the Netherlands (Netherlands) where one of the biggest petrochemical centers in Europe, as well as, the largest port are located, the Kingdom of Saudi Arabia (Saudi Arabia) where methanol production price is the lowest globally (Boulamanti and Moya, 2017), the People's Republic of China (China) which is the biggest methanol and cement producer and the second largest maize producer (Zhao and Yang, 2019), and the United States of America (USA) the biggest maize producer.

Renewable energy, water, land, and carbon sources per country are shown in Table 3. We included the current production of solar energy per country, as well as the potential solar energy. In all countries, solar energy potential has not been unlocked. Regarding water, we compared the renewable surface and groundwater to the consumption in the country. For land, we focused on the potential development of more agricultural land. Then, the total production of methanol to satisfy the production rate per country of methanol and HVC. The specific production of methanol and HVC per country is included in the Supplementary Material section S4.

Each country has specific conditions and circumstances. For example, the Netherlands is a country intensely spatially planned, where all of the surface of the country has already been allocated a purpose. Therefore, the development of land for maize production will not be possible. Between 2013 and 2020, 244 km² of agricultural land have

disappeared (CBS, 2022b). This situation puts even more pressure on land use.

Saudi Arabia is a water-scarce country where 60% of the water demand is satisfied via water desalination (Alnajdi et al., 2020). Furthermore, the climatic conditions of the country are not ideal for the growth of maize. The maize self-sufficiency of the country is less than 2% (Al-Nashwan et al., 2019). On the bright side, this country receives high solar irradiation (8 $\frac{GJ}{m^2*year}$) having a high potential for the production of renewable electricity.

China produces 81% of the total global methanol production. If this country keeps its chemical production rate, the demand for resources in this location is bigger compared to the other countries. China is a big country where the climate conditions vary on location. The northeast, where most of the cement industry is located, is a dry area. The south of China is where most of the country's water is located. Nonetheless, China is already facing water scarcity in this area, where maize is being produced (Meng et al., 2016). Furthermore, the accelerated reduction of agricultural land due to industrialization and urbanization represented a loss of 3024 km² in 2017 (Fei et al., 2021). These challenges in China make maize a not viable option in the production of maize as a carbon source. On the other hand, CO_2 emissions from cement are an abundant source of carbon. These emissions represent 50% of the global CO_2 cement emissions.

The USA is a resource-rich country. All the resources required to produce methanol and methanol for HVC are available; water, renewable energy, and land. This is the only country, from the four analyzed countries, where agricultural land has been extended. Every year between 2008–2016, agricultural land has been extended 4046 km² (Lark

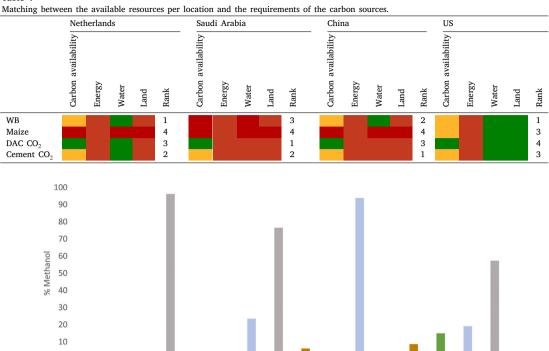


Fig. 7. The amount of methanol that can be produced based on the availability of carbon per location.

DAC CO2

Naste Biomass

Cement CO2

China

DAC CO2

Waste Biomass

Cement CO2

Maize

Saudi Arabia

et al., 2020). Therefore, this country has no limitations on the production of methanol either using biomasses or CO2 from the air.

Naste Biomass

Cement CO2

Netherlands

DAC CO2

Naste Biomass

0

3.5.1. Suitability of carbon sources per location

The suitability of a carbon source per location is showed in Table 4. In the Netherlands, maize is not an option as a carbon source due to the lack of available land. WB is the best option because it requires the least resources but there is not enough to supply all the carbon demand, so a combination of DAC CO2 and CO2 from the cement is needed. In Saudi Arabia, neither WB and maize are considered. Biomasses require more water than captured CO2 and since in this location water availability is very low, they are not suitable. In China, CO₂ from the cement is given the priority because it could supply almost all the carbon demand and requires less water compared to maize and WB. Maize is not included as a carbon source due to the none availability of land and the water scarcity in China. The USA is the only country were the availability of land make possible the consideration of maize.

Fig. 7 shows the contribution of each carbon source in percentage per location. The 100% represents the amount of methanol, light olefins, and aromatics produced in each country (this information can be found in the Supplementary Material section S4). DAC CO₂ is required in three out of the analyzed countries. China is the only country where cement CO2 provides more than 90% of the carbon demand. This is due to the global centralization of cement production, yet waste biomass is also considered thanks to its lower energy demand and the water availability in the country. In all the analyzed locations, DAC CO2 is needed to supply the carbon demand for the production of methanol.

4. Discussion

4.1. DAC will be the only carbon source in the long term while the cement industry could be a transition source

Cement CO2

DAC CO2

The substitution of fossil carbon in the chemical industry could only be satisfied by DAC CO₂. Biomasses could produce a small percentage of the total carbon demand. CO2 from the cement industry could provide almost all the demand for carbon in China. Nevertheless, it is envisioned that China will transform the cement industry into a lowcarbon industry by 2060 (Zhao et al., 2022; Dinga and Wen, 2022). This might be achieved by powering the process by using renewable electricity and substituting the CO₂ emitting raw material (limestone) for industrial solid waste as carbide calcium (Zhang et al., 2021a) or waste from the iron and steel industry as blast furnace slag or fly ash (Tan et al., 2022). Therefore, in the short term, the cement industry would be the main source of carbon but as the envisioned carbon neutrality would be achieved, CO2 from the air would become a stronger carbon supplier.

4.2. The availability of renewable energy determines the production of defossilized methanol

The energy demand to produce the current demand for methanol and methanol for HVC from DAC CO2 would be 60 EJ. Renewable energy production reached 80 EJ in 2019 (IEA, 2020). The growth rate of renewable energies during 2009–2019 period was $13.4 \frac{\%}{\text{year}}$ and the energy demand has increased $1.8\frac{\%}{\text{year}}$ in the same period (Holechek et al., 2022). Therefore, if we would like to defossilize the chemical industry by 2030, we would need an extra 16% yearly increase in the growth rate of renewable energies. These high increases in the supply of renewable energy were also estimated by Kätelhön et al. (2019). Where in order to use captured $\rm CO_2$ to defossilize the chemical industry an increase of 126% and 222% of the estimations for 2030 by the IEA are needed.

The use of DAC CO $_2$ as a source of carbon demands a great amount of energy, where more than 70% of the energy demand in the production of methanol is for the production of hydrogen. The theoretical energy of hydrogen is 286 $\frac{kJ}{\text{mol}_{\text{H2}}}$ and the best available technology demands 379 $\frac{kJ}{\text{mol}_{\text{H2}}}$. Even if the theoretical values for H $_2$ and CO $_2$ capture would be used in the calculations, still 28 $\frac{GJ}{\text{tonmeoh}}$ is needed. This saves 10 GJ energy compared to the value calculated for the current best technologies. So it is important to further develop the technologies. However, even then the energy demand for methanol production is 1.4 times higher than the energy demand of producing methanol from methane/coal and thus big investments in renewable energy are always required.

4.3. Location change in the production of defossilized methanol

The production location of defossilized methanol would be dependent on the availability of renewable energy. This requirement does not limit the availability of DAC CO_2 , since it is independent of location compared to the other carbon sources analyzed.

The potential production of solar energy is more favorable in high solar irradiance countries such as Saudi Arabia where the solar irradiation can reach 10 $\frac{GJ}{m^2*year}$ (Aldhubaib, 2022) than in the Netherlands where the irradiation can reach 3.9 $\frac{GJ}{m^2*year}$ (Laevens et al., 2021). Consequently, the production location of defossilized methanol would be in countries where there is a high availability of renewable energy.

For the energy supply, we assumed solar energy as renewable energy to produce methanol in each of the analyzed countries. Nevertheless, other renewable energies such as wind energy could also be considered, broadening the availability of renewable energy. The distribution of methanol from high-potential renewable energy countries is favorable compared to the distribution of hydrogen (Schorn et al., 2021). This is due to the fact that methanol density is almost 800 times greater than the density of hydrogen. Therefore, methanol has even a greater potential to be produced over hydrogen. A production shift of methanol could be expected from fossil-rich countries to countries with high renewable energy production.

5. Conclusion

In this research, we analyzed the implications of substituting fossil carbon to different defossilized carbon sources in the production of methanol. From the analyzed carbon sources (maize, WB, DAC CO $_2$, and CO $_2$ cement), biomasses require the least energy (44–54%), but they required the most water and land demand (27–650%), compared to captured CO $_2$. While captured CO $_2$ require the least water and land but they do require the most energy. The use of these defossilized carbon sources could be done but it will depend on the availability of resources per location. In all the analyzed locations (Netherlands, Saudi Arabia, China, and the USA), DAC CO $_2$ contributes to the demand of carbon. This is because DAC CO $_2$ requires the least water and land and it is highly available. Renewable energy availability is critical to harness DAC CO $_2$, therefore, the production of defossilized chemicals could be determined by the availability of renewable energy per location and not the availability of fossil fuels as it is nowadays.

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CRediT authorship contribution statement

Ivonne Servin-Balderas: Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. Koen Wetser: Writing – review & editing, Supervision, Conceptualization. Cees Buisman: Writing – review & editing, Supervision. Bert Hamelers: Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

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

Data availability

No data was used for the research described in the article.

Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.jenvman.2024.120304.

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