Supplementary information for:

Environmental Consequences of Alternative Fuels for the Maritime Transportation Sector

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# S1: Description of fuel pathways

A diagram of a company

Description automatically generated

Figure S1: Summary of pathways for fuel production

*Very low-sulphur fuel oil (VLSFO)*

In this study, VLSFO is a fossil fuel used as the reference fuel. VLSFO is produced via desulphurisation of crude oil, where the final product contains only 0.1% sulphur, thus complying with IMO sulphur regulations. In this process, hydrogen is required for hydrotreating [1]. It is assumed that the hydrogen used comes from steam methane reforming (SMR) of natural gas. The hydrotreating process results in a desulphurised oil stream (VLSFO), as well as a naptha by-product and hydrogen sulphide (H2S). The naptha by-product is assumed to substitute diesel. The H2S stream is then treated, resulting in a fuel gas and elemental sulphur and sulphur dioxide (SO2) emissions [1]. The resulting VLSFO product is then transported by pipeline to the port.

*Liquefied natural gas (LNG)*

Liquefied natural gas (LNG) is considered a promising transition fuel for the sector due to the availability of feedstock (natural gas), existing infrastructure for production and distribution, and lower CO2, SOx, NOx and PM emissions compared to conventional fuel oils (e.g. VLSFO). LNG is produced by the extraction, dehydration, desulphurisation and liquefaction of natural gas. During the processing and distribution of LNG, methane leakage occurs with values between 0.22% and 3.9% [2–4]. LNG is then transported by pipeline to the port.

*Conventional ammonia with CCS*

Ammonia produced from natural gas coupled with carbon capture and storage is designated ‘blue ammonia’. This fuel has been identified as a potential key fuel for the maritime sector due to the availability of natural gas, existing technology and infrastructure for production, and lower cost compared to e-fuels . In this process, natural gas is reformed by steam methane reforming (SMR), autothermal reforming (ATR), and the water-gas shift reaction [3,5] to produce ammonia. The CO2 produced in the SMR process can be captured by a number of means, although in this study only chemical absorption is considered. The carbon capture rates are between 90-95% using MEA, MDEA or methanol as solvents [3,6–10]. The solvent for carbon capture is taken as 'market for monoethanolamine, GLO' from ecoinvent [11]. In addition to the CO2 captured from the syngas, the CO2 in the flue gas from heat production is also captured by chemical absorption, which requires an additional electricity input [7]. The captured carbon is sent to geological storage, following work done by Mayer et al. (2023) and Shu et al. (2023). The liquid ammonia product is sent to the port via pipeline. Heat is produced and used to substitute marginal heat.

*E-ammonia*

E-ammonia is produced by combining e-hydrogen and nitrogen from air. For e-hydrogen production, the data for the parameters for electrolysis were taken for PEM, SOEC and AEC electrolysers, where the electricity demand is between 30-90 kWh/kg hydrogen. The source of electricity was considered as wind electricity. Excess heat is also released, and could be recovered for use in district heating, but this is not modelled [12]. Capital goods for the electrolysis unit were taken from [3,13,14], which is based on a PEM unit, but it is estimated that similar materials are required for all units, and lower and upper ranges of material requirement were found based on ranges for stack lifetime and efficiency.

The nitrogen is obtained by cryogenic air separation. Currently, cryogenic air separation is mainly used to produce pure oxygen, with the nitrogen being emitted to air as a waste product. However, the expected increase in demand for nitrogen for ammonia production means that ASU units will likely be built and installed specifically for the purpose of ammonia production, and thus the construction of this unit is modelled. The oxygen is assumed to be emitted to the air, although in the future is could be sold. The hydrogen and nitrogen are then combined in the Haber Bosch process, in a 3:1 molar ratio [3,5,15]. After production, liquid ammonia is sent via pipeline to the port.

*E-methanol with direct air capture (DAC)*

E-methanol with DAC comprises electrolysis of water to produce e-hydrogen, direct capture of CO2 from the air, and a methanol synthesis step. The e-hydrogen production is the same as for e-ammonia. The DAC unit is based on literature from [16–20], and the capital goods based on [21]. After methanol synthesis, the methanol is sent by pipeline to the port.

*E-methanol with biogenic carbon capture (hybrid methanol)*

E-hydrogen can also be combined with biogenic CO2 to form e-methanol. The sources of this CO2 can be from biogas plants or gasification of biomass, with the latter being the focus of this study. The gasification plant is modelled the same as for biomethanol, and it is assumed that the methanol produced by the plant contributes to the final methanol product. A small amount of monoethanolomine solvent, as well as electricity, is required to capture the CO2 for use in the e-methanol production.

*Biomethanol*

Biomethanol can be produced via biogas or direct biomass gasification, and in this study the latter is investigated. The data for the bio-methanol process is taken primarily from Poluzzi et al. (2022) and Yadav et al. (2020) [22,23]. Feedstock type for gasification can vary, but woody biomass is chosen for this study. In the gasification process, wet biomass is dried to between 10-15% moisture content [22]. Dried biomass is then gasified using oxygen as a gasifying agent [24] to produce a crude syngas, with biochar as a byproduct [22]. Pure oxygen is preferred over air, as the use of air results in a large volume of inert nitrogen flowing through the system [25] although the technologies to obtain pure oxygen can be expensive. During the gasification process, CO2, PM, NOx and N2O are released. The syngas from gasification must be cleaned, which can be achieved by autothermal reforming. Methanol can then be synthesized on a nickel catalyst, and purified by distillation. The methanol product is sent to the port by pipeline.

Table S 1: Balance of CO2 release and uptake over the biomethanol fuel life cycle.

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter | Unit | Amount | Reference |
| C content in biomass | kgCO2/kg dry biomass | 0.48 | [23,26,27] |
| Biomass in | kg dry biomass/MJ | 0.16 | [23] |
| **CO2 uptake by biomass** | **kgCO2/MJ shaft power** | **0.28** | **Calculated** |
| CO2 released (gasification) | kgCO2/MJ shaft power | 0.14 | [27] |
| CO2 released (combustion) | kgCO2/MJ shaft power | 0.14 | [2,18,28–35] |
| **CO2 released (total)** | **kgCO2/MJ shaft power** | **0.28** | **Calculated** |

*Dimethyl ether (DME)*

DME is an attractive alternative fuel because of its clean-burning properties: combustion of the fuel results in nearly no PM emissions, and lower NOx and CO emissions compared to diesel or natural gas [27,36,37]. Additionally, DME has a slightly higher LHV than methanol (27.6-28.9 MJ/kg) [27,36–38]. DME can be produced directly from fossil resources, such as natural gas and coal [36,39], or from biomass [27,40]. More indirectly, methanol produced via any pathway can be dehydrated to form DME [41]. In this study, DME is produced by dehydration of biomethanol, where methanol is produced as described above. The DME synthesis step requires additional heat and electricity for dehydration.

Table S 1: Balance of CO2 release and uptake over the DME fuel life cycle.

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter | Unit | Amount | Reference |
| C content in biomass | kgCO2/kg dry biomass | 0.48 | [23,26,27] |
| Biomass in | kg dry biomass/MJ | 0.19 | Calculated |
| **CO2 uptake by biomass** | **kgCO2/MJ shaft power** | **0.33** | **Calculated** |
| CO2 released (gasification) | kgCO2/MJ shaft power | 0.17 | Calculated |
| CO2 released (combustion) | kgCO2/MJ shaft power | 0.15 | [30,32] |
| **CO2 released (total)** | **kgCO2/MJ shaft power** | **0.33** | **Calculated** |

*Pyrolysis oil via fast pyrolysis*

Fast pyrolysis involves the high-temperature decomposition of biomass over a short period of time, between 1-5 seconds [12]. A variety of feedstock types can be used, but in this study, only woody biomass was examined. Pre-treatment by drying and chipping is included in the system boundaries, and after pyrolysis, the bio-oil is upgraded by hydrotreating and hydrocracking [42–44], resulting in diesel and gasoline fractions that can be used as maritime fuels. The by-products from the system are biochar and gas, although all of the gas and between 60-100% of the biochar is assumed to be used for internal energy generation in the process [42,44,45]. The remaining biochar has a carbon content similar to coal [45] and can be extracted and combusted for energy [26] or used on land for carbon storage and soil remediation [46]. Hydrogen is required for the bio-oil upgrading, and this is assumed to be from steam methane reforming (SMR). After upgrading, the gasoline and diesel fractions are sent via pipeline to the port.

Table S 1: Balance of CO2 release and uptake over the pyrolysis oil (via fast pyrolysis) fuel life cycle.

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter | Unit | Amount | Reference |
| C content in biomass | kg CO2/kg dry biomass | 0.48 | [23,26,27] |
| Biomass in | kg dry biomass/MJ | 0.17 | [42,43,45,47] |
| **CO2 uptake by biomass** | **kgCO2/MJ** | **0.30** | **Calculated** |
| CO2 released (pyrolysis) | kgCO2/MJ | 0.10 | [42,45] |
| C stored (biochar) | kgC/MJ | 0.01 | [42–44,47] |
| CO2 released (combustion) | kgCO2/MJ | 0.14 | [32,48] |
| **CO2 released (total)** | **kgCO2/MJ** | **0.30** | **Calculated** |

*Pyrolysis oil via slow pyrolysis*

Slow pyrolysis is similar to fast pyrolysis, although at lower temperatures (500-600°C) and over a longer period of time, typically between 5 and 20 minutes, resulting in a lower bio-oil yield but higher biochar and gas yields [12]. In this scenario, straw residue is used as the feedstock. The pre-treatment for this includes drying to 10% moisture content and pelletizing [12]. It is assumed that the bio-oil undergoes the same upgrading process as oil from fast pyrolysis. As a result of higher gas yields, heat is produced by the system, which is assumed to substitute heat from steam.

Table S 1: Balance of CO2 release and uptake over the DME fuel life cycle.

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter | Unit | Amount | Reference |
| C content in biomass | kgCO2/kg dry biomass | 0.42 | [49] |
| Biomass in | kg dry biomass/MJ | 1.03 | [12,50] |
| **CO2 uptake by biomass** | **kgCO2/MJ** | **1.60** | **Calculated** |
| CO2 released (pyrolysis) | kgCO2/MJ | 0.27 | [42,45] |
| CO2 out (pyrolysis gas) | kgCO2/MJ | 0.15 | [12,50] |
| C stored (biochar) | kgCO2/MJ | 0.28 | [12,50] |
| CO2 released (combustion) | kgCO2/MJ | 0.14 | [32,48] |
| **CO2 released (total)** | **kgCO2/MJ** | **1.60** | **Calculated** |

## Data sources for fuel production

Table S 2: Summary of data sources used for fuel production inventory

|  |  |  |
| --- | --- | --- |
| **Fuel pathway** | **ID in database** | **References for fuel production** |
| VLSFO | VLSFO | [1] |
| LNG | LNG | [2–4,11] |
| Ammonia with CCS | NH3\_CCS | [1–4,6–11,51–53] |
| e-Ammonia | eNH3 | [3,11,13–15,17,18,54–58] |
| e-Methanol with DAC | eMeOH\_DAC | [11,13,14,16–20,35,54–57,59] |
| Hybrid methanol | eMeOH\_bio | [11,22,23,29] |
| Biomethanol | bioMeOH | [11,22,23,29] |
| DME | DME | [11,22,23,29] |
| Pyrolysis oil (fast) | PO\_fast | [12,42–45,47] |
| Pyrolysis oil (slow) | PO\_slow | [12,42–44,47] |

## Data sources and representation for fuel combustion

Table S 3: Summary of data sources used for fuel combustion inventory

|  |  |  |
| --- | --- | --- |
| **Fuel** | **ID in database** | **References** |
| VLSFO | VLSFO\_combustion | [31,60,61] |
| LNG | LNG\_combustion | [2,28–31,33,34,48,61–70] |
| Ammonia | NH3\_combustion | [18,28,61,71,72] |
| Methanol | MeOH\_combustion | [2,18,28–31,33–35,61] |
| DME | DME\_combustion | [39,61] |
| Pyrolysis oil | PO\_combustion | [61,73,74] |

Figure S2 shows the number of values reported in the data sources used for each emission per fuel type. As with the values for the life cycle inventory for fuel production, the geometric mean and geometric standard deviation of these emission values were taken for the life cycle inventory of the fuel combustion phase.

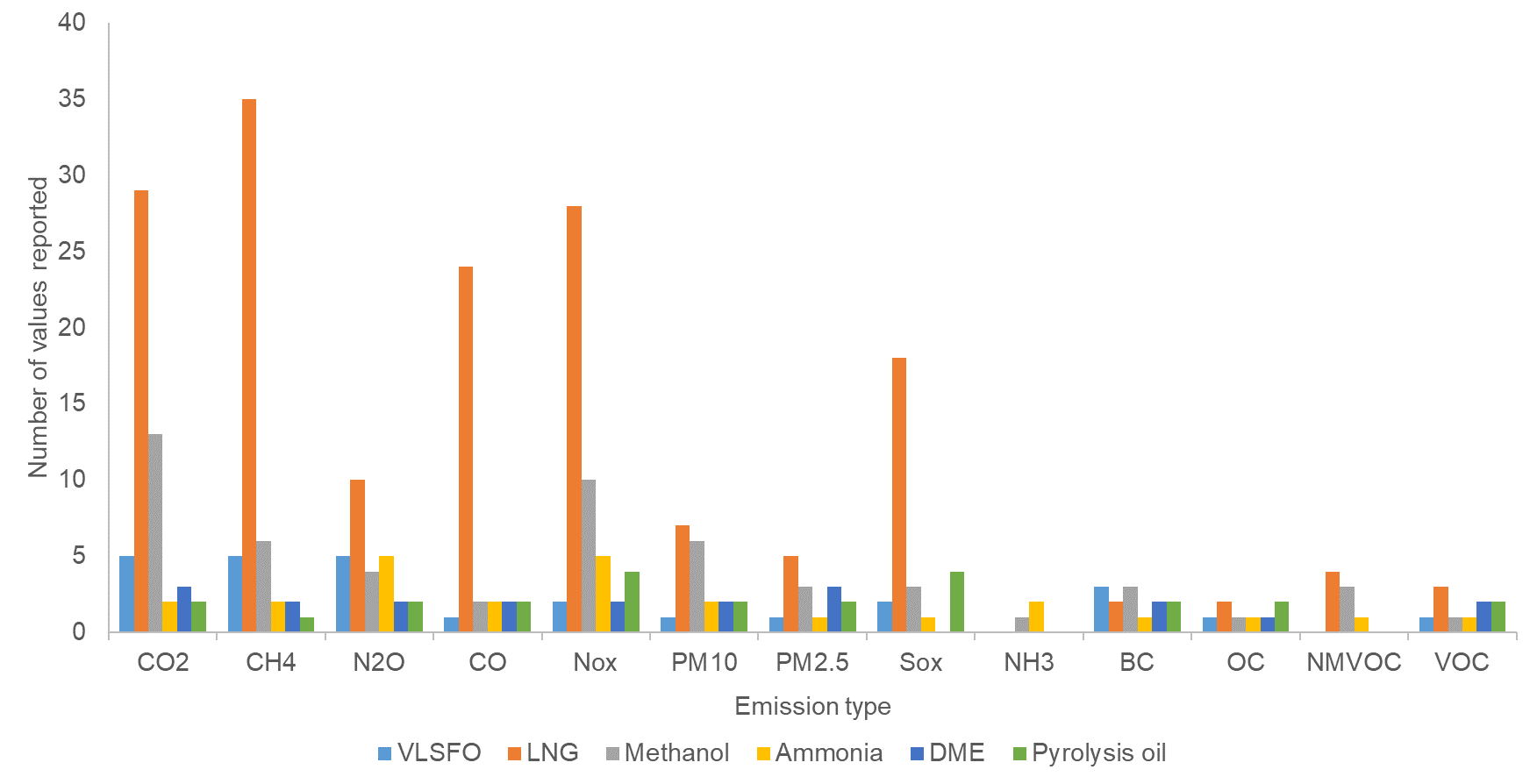


Figure S2: Representativeness of emissions from combustion for each fuel type

In order to calculate the LCI for the first functional unit, the specific fuel consumption (SFC) is required. This value is the amount of fuel required to provide one kWh of energy to the shaft, and thus accounts for both the energy density of the fuel and engine efficiencies. In some cases, multiple values for the SFC were found, and the geometric mean was taken. For the calculation of the LCI for the second functional unit, the efficiency of the vessel (i.e. how much power is required to transport the cargo) is required. As this study aims to examine a range of engine and vessels, this was calculated according to how much additional storage space (and therefore number of trips) are required to fulfil the same work as VLSFO. The average vessel efficiency for an 8000 - 12000 TEU container ship running on fuel oil is 0.12 MJ/t-km [75]. For LNG, ammonia and methanol, the cargo capacity is reduced by 3.6%, 4.14% and 3.4% [29,64,76,77]. DME is assumed to be reduced by the same amount as methanol due to its similar properties, and pyrolysis oils are not assumed to reduce cargo capacity, as they are upgraded to diesel and gasoline fractions. These cargo capacity reductions were used to calculate vessel efficiencies for the alternative fuels. Table S3 shows the values for the LHV, SFC and vessel efficiency for all the fuel types.

Table S4: The lower heating value (LHV), specific fuel consumption (SFC) of the different fuels and vessel efficiency for all the fuels assessed in this study.

|  |  |  |  |
| --- | --- | --- | --- |
| **Fuel pathway** | **LHV**  **(MJfuel/kgfuel)** | **SFC**  **(gfuel/kWhshaft power)** | **Vessel efficiency (MJshaft power/t-km)** |
| VLSFO | 41.2 | 167 | 0.120 |
| LNG | 46.5 | 150 | 0.124 |
| Ammonia | 19.0 | 380 | 0.125 |
| Methanol | 19.9 | 353 | 0.124 |
| DME | 28.9 | 280 | 0.124 |
| Pyrolysis oil | 42.0\* | 205 | 0.120 |

\*Because the pyrolysis oil is upgraded into diesel and gasoline fractions, the LHV values for diesel and gasoline are taken.

# S2: Sensitivity analysis of biomass counterfactual

## Baseline scenario (decay)

The composition of the forestry residues was taken for pine residues and pine stems, with a carbon content of 47-50% [23,26,27]. For straw residues, the carbon content was taken as 41-44% [49]. The additional CO2e factor used to correct for the difference in timing of emissions was taken from Petersen et al. [78], Tonini et al. [79] and Schmidt et al. [80], which, when corrected for carbon content, yielded factor values between 0.076-0.11 kgCO2/kg forestry residues and 0.047-0.067 kgCO2/kg straw residues.

In addition, the decay of biomass on land results in NOx, N2O, NH3 and NO3, and thus removing these residues and converting them to fuel results in avoidance of these emissions. However, it also prohibits the return of nutrients to the soil, which must be offset by additional fertiliser application in the case of straw residues.

## Biomass used for electricity and heat

Table S 5: Data used for modelling of electricity and heat production from forestry and straw residues

|  |  |  |  |
| --- | --- | --- | --- |
| **Forestry residues** | | **Straw residues** | |
| Value | Reference | Value | Reference |
| *Electricity potential (kWh/kg dry biomass)* | | | |
| 1.11 | [81] | 1.11 | [81] |
| 1.32 | [80] | 1.52 | [80] |
|  |  | 1.47 | [82] |
|  |  | 1.01 | [83] |
| *Heat potential (MJ/kg dry biomass)* | | | |
| 14.6 | [84] | 10 | [84] |
| 11.2 | [81] | 11.2 | [81] |
|  |  | 8.66 | [83] |

# S3: Biochar

The production of biomethanol and the pyrolysis oils results in a biochar by-product. Biochar is gaining attention due to its potential for carbon storage or soil remediation [42,46,85,86], although the potential uses and benefits of biochar are as yet uncertain. As a baseline scenario, biochar was assumed to substitute the processing and use of hard coal, as it can be burnt and used for energy, considering the similar energy densities of coal and biochar [46,85]. It is seen from Figure 3J in the main text that the substitution of hard coal by the biochar is what offsets the climate change impact of pyrolysis oil via slow pyrolysis, and changing the use of the by-product could affect the LCA results. Three alternative uses of the biochar were examined in this sensitivity analysis: lime, which can be used to increase the pH of soil, silica sand, which is used as an adsorbent for wastewater treatment, and the use of biochar a carbon sink (left on land). For the latter, it was assumed that 80% of the carbon in the biochar can be sequestered for 100 years, while 20% decays over this period [86]. Figure S3 shows the climate change impact scores of these three alternative uses.

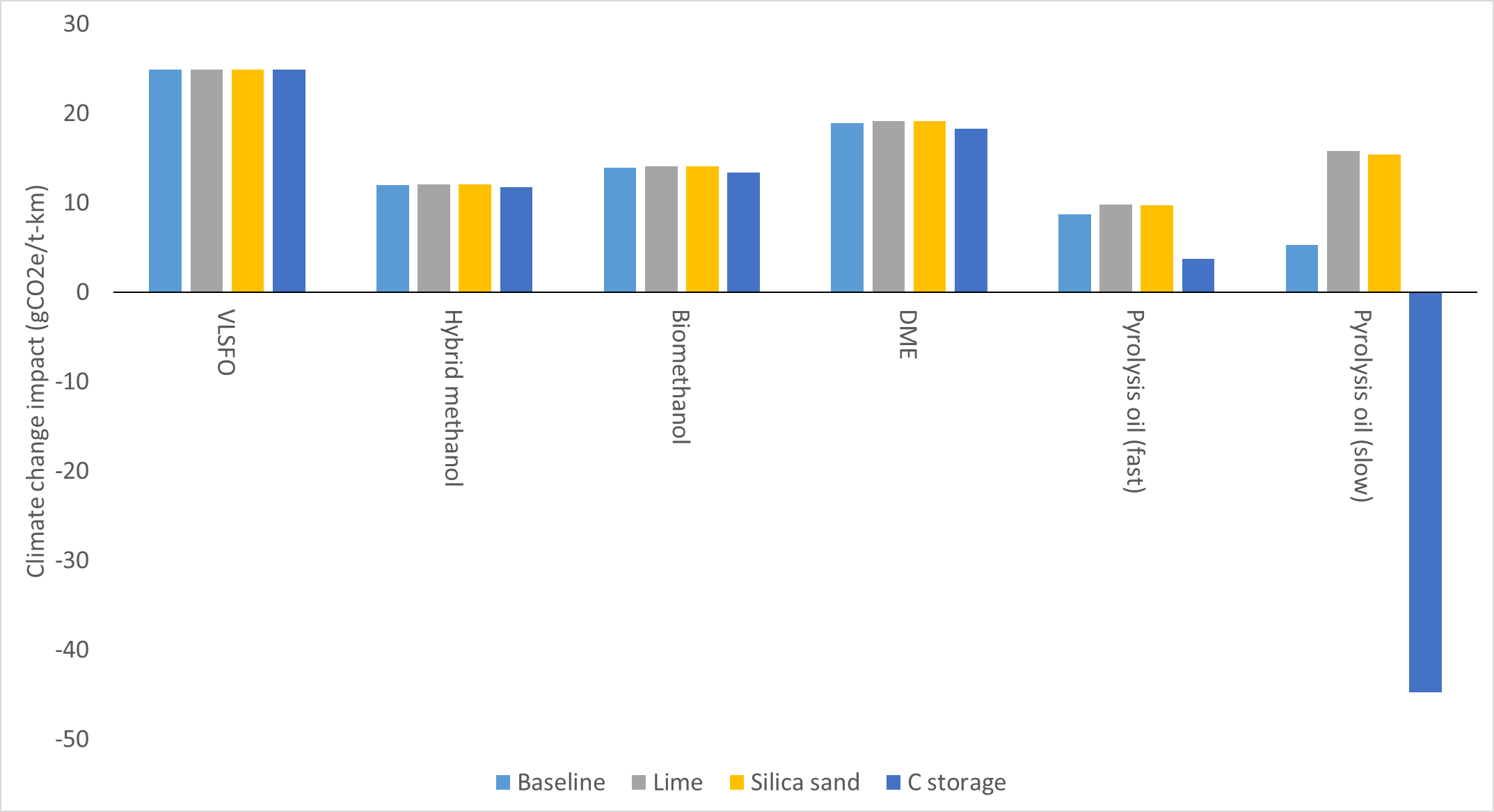


Figure S3: Climate change impact scores for the biofuels for different biochar use scenarios.

For pyrolysis oil from slow pyrolysis, biochar is the main product of the pyrolysis process (with 4.8 kg biochar being produced per kg pyrolysis oil). If this biochar is used to substitute hard coal for energy or other purposes, the potential offset is substantial. If this biochar is used for other purposes, like substituting lime or silica sand, which do not have as high a climate change impact as coal, then the savings are not as large. The largest saving is from the use of biochar as a carbon sink in the case of slow pyrolysis. If, instead of combusting the biochar in place of coal, the biochar remains as a storer of carbon, the production of pyrolysis oil via slow pyrolysis could result in a negative climate change impact, which is in line with other studies [87,88]. However, it is reiterated that this is only the case where the biomass for the pyrolysis oil production is not in use for heat and electricity production.

# S4: Calculation of RED carbon intensity scores

For the calculation of the carbon footprint according to the RED guidelines, the following equation was used:

|  |
| --- |
|  |

Where:

|  |  |
| --- | --- |
| E = | The total emissions from the use of the fuel (i.e. the CI score) |
| = | The emissions from the extraction/cultivation of raw materials |
| = | The emissions as a result of land use changes |
| = | The emissions from fuel processing (e.g. electricity, heat, chemicals, etc.) |
| = | The emissions from transporting the fuel and/or raw materials |
| = | The emissions from combustion of the fuel |
| = | Emission savings from soil carbon accumulation due to improved agricultural practices |
| = | Emission savings from capture and permanent storage of CO2 |
| = | Emission savings from capture of biogenic CO2 to replace fossil CO2 in other production processes |

The biofuels assessed in this study are derived from forestry and agricultural residues. According to the RED, these are considered burden-free, and as such *ec* is zero. For biomethanol and DME from forest residues, default values are provided in the RED, and these were used. For e-hydrogen production, the requirements according to the Delegated Act of a direct connection to a renewable electricity source, which is assumed in this study, results in an emission factor of zero for the wind turbine. Capital goods are not considered under the RED.

The flows (amounts) were taken from the LCI, and emission factors taken from ecoinvent 3.9.1 cutoff [11]. These are shown in Table S5:

Table S 6: Data used for calculation of RED carbon intensity scores

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Fuel/  Input | Parameter | Unit | Amount (per kg) | EF (gCO2e) | GWP |
| eH2 | Electricity | kWh | 48.7 | 0.00 | 0.00 |
| Water | kg | 8.95 | 5.48 | 49.11 |
| Transport | tkm | 0.10 | 12.80 | 1.28 |
| **Total** | **gCO2e** |  |  | **50.39** |
|  |  | **gCO2/MJ fuel** | |  | **0.42** |
| eMeOH DAC | eH2 | kg | 0.20 | 50.4 | 9.85 |
| Electricity | kWh | 1.47 | 346.6 | 509.06 |
| Heat | MJ | 7.81 | 75.0 | 585.87 |
| Solvent | kg | 0.004 | 1115 | 4.18 |
| Transport | tkm | 0.10 | 12.8 | 1.28 |
| **Total** | **gCO2e** |  |  | **1110.23** |
|  | **gCO2/MJ fuel** | |  | **55.79** |
| eNH3 | eH2 | kg | 0.18 | 50.39 | 8.99 |
| Electricity | kWh | 1.56 | 346.58 | 540.29 |
| Water | m3 | 0.16 | 0.43 | 0.07 |
| Transport | tkm | 0.10 | 12.80 | 1.28 |
| **Total** | **gCO2e** |  |  | **606.43** |
|  | **gCO2/MJ fuel** | |  | **31.92** |
| Hybrid MeOH | eH2 | kg | 0.01 | 50.39 | 0.47 |
| Electricity | kWh | 0.08 | 346.58 | 28.96 |
| Biomethanol | kg | 0.52 | 268.65 | 138.65 |
| Transport | tkm | 0.10 | 12.80 | 1.28 |
| **Total** | **gCO2e** |  |  | **169.35** |
|  | **gCO2/MJ fuel** | |  | **8.51** |
| PO\_fast | Biomass in | kg | 2.98 | 0.00 | 0.00 |
| Residues transport | tkm | 0.30 | 148.71 | 44.30 |
| Electricity | kWh | 0.40 | 346.58 | 139.56 |
| Natural gas | m3 | 0.35 | 593.63 | 204.87 |
| Transport | tkm | 0.10 | 12.80 | 1.28 |
| **Total** | **gCO2e** |  |  | **390.02** |
|  | **gCO2/MJ fuel** | |  | **9.51** |
| PO\_slow | Biomass in | kg | 1.80 | 0.00 | 0.00 |
| Residues transport | tkm | 0.18 | 148.71 | 26.75 |
| Electricity | kWh | 0.92 | 346.58 | 319.58 |
| Natural gas | m3 | 0.29 | 593.63 | 169.61 |
| Transport | tkm | 0.10 | 12.80 | 1.28 |
| **Total** | **gCO2e** |  |  | **517.22** |
|  | **gCO2/MJ fuel** | |  | **12.62** |

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