

Review

Bio-CO₂ as Feedstock for Renewable Methanol in Maritime Applications

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Abstract

Bio-CO₂ is part of the natural carbon cycle and represents a sustainable carbon source for the production of Renewable Fuels of Non-Biological Origin (RFNBOs), such as synthetic methanol. This study addresses the critical knowledge gap in aligning diverse biogenic CO₂ sources with e-methanol requirements in the EU by providing harmonized mapping, based on datasets, literature sources, and reported industrial statistics at the sectoral and country level. Bio-CO₂ streams from biogas and biogas upgrading, biomass combustion, pulp and paper, bioethanol production, and the food and beverage sector are evaluated for total emissions, CO₂ concentrations and purity, the geographical distribution, seasonality, and impurity profiles. Results show that approximately 350 Mtpa of bio-CO₂ are emitted across the EU, with highly heterogeneous characteristics. Biogas upgrading and fermentation-based processes generate highly pure CO₂ streams (>98–99%), yet their small and dispersed nature complicates logistics. In contrast, biomass-combustion and pulp and paper sectors provide large volumes (around 214.6–298.2 Mtpa and 73.9 Mtpa CO₂, respectively), but in diluted streams (typically 3–15% and 10–20%). Replacing just 10% of the EU maritime fuel demand with e-methanol would require 53.6 Mtpa of bio-CO₂ and 58 GW of electrolyzer capacity, a stark contrast to the current operational 385 MW. The findings highlight the need for infrastructure planning and aggregation hubs to enable the large-scale deployment of RFNBO methanol in the maritime sector.

Keywords: biogenic CO₂; carbon capture and utilization; RFNBO; methanol; maritime decarbonization; renewable hydrogen; maritime fuels



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1. Introduction

According to the International Maritime Organization (IMO), the shipping industry contributed around 3% of the world's CO₂ emissions in 2018. In response, a strategy was approved by the IMO to cut greenhouse gas (GHG) emissions from ships. The goal was set to achieve net-zero emissions by 2050. This strategy was revised in 2023, to provide more ambitious targets, including achieving net-zero emissions close to 2050 and promoting the adoption of zero or near-zero alternative fuels [1]. At present, the maritime sector mainly relies on various types of fuels for propulsion and power generation, with the majority being fossil fuels [2]. Fuel selection depends on factors like the operational patterns, size, vessel type, regulations, and availability. Heavy fuel oil, marine diesel oil, and marine

gas oil are the most common maritime fuels used, with alternative options encompassing methanol, Liquefied Natural Gas (LNG), Liquid Petroleum Gas (LPG), biofuels, ammonia, and hydrogen. In certain instances, these fuels can be used as “dual fuels”, blended with a portion of conventional fuel to enhance ignition performance [3].

Certain alternative fuel options, including methanol and LNG, are derived from carbon sources, and vessels opting for these carbon-based fuels may potentially incur emission fees. Within the European Union’s Emissions Trading System (ETS), ships using carbon-based fuels are obliged to acquire carbon credits to offset emissions generated during voyages to and from Europe, regardless of the origin. Despite potentially lower emissions compared to vessels powered by conventional fuels, carbon-based alternative fuels are often regarded as interim measures, with non-fossil carbon sources like biomass being perceived as potentially more sustainable in the long-term [4,5]. In this broader decarbonization context, increasing attention is being paid to Renewable Fuels of Non-Biological Origin (RFNBOs). RFNBOs are fuels produced from renewable electricity and non-fossil carbon sources, in accordance with EU regulatory definitions, and include synthetic fuels such as e-methanol produced from renewable hydrogen and captured CO₂. When the CO₂ originates from biogenic sources or from the atmosphere and hydrogen is generated via renewable electricity, RFNBO methanol can achieve very low or near-zero life-cycle greenhouse gas emissions, depending on system boundaries and accounting methodologies.

In pursuit of this objective, this work is investigating the potential of incorporating bio-CO₂ resources in conjunction with renewable hydrogen to produce methanol tailored for maritime applications. Biogenic CO₂ emissions refer to those naturally occurring within the carbon cycle or arising from various processes like combustion, fermentation, or digestion. When biomass is combusted, the carbon released is part of the biogenic carbon cycle, essentially returning to the atmosphere the carbon previously absorbed by plants during their growth. This is the difference compared to fossil CO₂ emissions, which originate from using fossil fuels and release carbon that has been sequestered underground over geological timespans, adding further stress to the carbon cycle. Figure 1 shows the two carbon cycles, presenting the biogenic, as well as the fossil-based, carbon cycle. Through the production of methanol using bio-CO₂ instead of fossil-derived CO₂ along with the incorporation of renewable hydrogen, it is anticipated that the production and utilization of methanol will not impose additional stress on the carbon cycle.

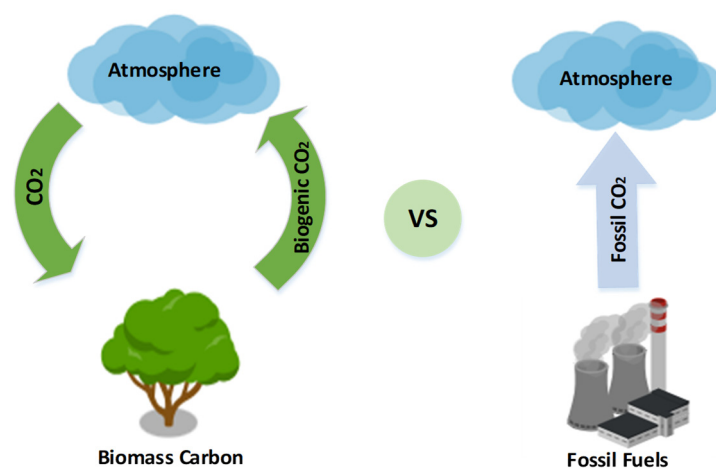


Figure 1. Biogenic and fossil CO₂ emissions carbon cycle.

Nowadays, the most common uses of CO₂ in the European Union are in the food and beverage (FAB) industry, urea production, fabrication of metals, and enhanced oil recovery (EOR) processes. It is estimated that 41 Mtpa of CO₂ is the annual CO₂ demand in the

EU, which corresponds to 16% of the global CO₂ demand and is mostly satisfied from fossil CO₂. Food and beverage industries consume around 16 Mtpa of CO₂, which is used for the carbonation of beverages, packaging, and stunning of animals. Urea production demanded around 7 Mt CO₂ in 2020, where its production is based on the ammonia reaction with CO₂. EOR accounts for 34% of the global CO₂ demand, but this is not especially prevalent for Europe since there are only two locations in Europe producing 2% of the oil produced globally via EOR, where the CO₂ demands of the process are around 2 Mtpa. Urea production and enhanced oil recovery are strongly linked to fossil fuels. However, the demand for CO₂ in EOR is expected to fall by 2050, along with a reduction in oil extraction inside the EU [6]. Emerging sectors for utilization and therefore potential uptakers of CO₂ are for chemical/fuel production [4,7] and concrete curing [8].

Methanol (MeOH, CH₃OH) is the simplest alcohol, possessing attributes that have garnered considerable interest for its application as both an energy source and a hydrogen carrier. Notably, methanol is soluble in water, is readily degradable, and is liquid under atmospheric conditions, facilitating its storage and transportation. In addition, MeOH exhibits similar characteristics to conventional marine fuels meaning that storage in existing fueling facilities requires minimal adjustments [9]. It can be stored in tanks equipped with floating roofs for larger scales and floating baffle tanks for smaller capacities, adhering to similar safety provisions as those for gasoline storage, including grounding requirements [10]. Consequently, the utilization of methanol necessitates relatively modest investments for adapting the storage, transportation, and refueling infrastructure compared to hydrogen [11]. Presently, methanol is accessible at over 120 ports globally, including EU ports like Antwerp and Rotterdam. While methanol is widely traded as a chemical feedstock, its current production is still largely based on natural gas and coal, underscoring the need to develop renewable and RFNBO-compliant methanol-production pathways [11,12]. For the large-scale adoption of methanol as a marine fuel, beyond storage considerations, a safe bunkering operation and a geographically widespread bunkering network are required. Furthermore, ship owners must have confidence in long-term fuel availability and economic competitiveness when committing to fuel-switching decisions [12]. Ensuring the sufficient availability of RFNBO methanol in ports therefore requires reliable access to suitable carbonaceous feedstocks, such as bio-CO₂ coupled with renewable hydrogen at an adequate scale and cost [13].

At the same time, there remains substantial uncertainty regarding the total volume of bio-CO₂ emissions available in the EU. This uncertainty stems from the heterogeneity of bio-CO₂-emitting sectors, inconsistencies in emissions reporting across countries and facilities, and variations in estimation methodologies across studies. In certain reports, the total European bio-CO₂ sector is estimated at approximately 500 Mtpa [14,15], whereas in a recent report by ERM, it was estimated that the potential usable EU bio-CO₂ is approximately 154–250 Mtpa [6]. Nevertheless, in all cases, critical aspects arise, directly related to whether it is feasible (technically and economically) to capture and use this CO₂ for the production of high-added value products such as methanol, as well as if the available bio-CO₂ quantities in the EU are sufficient to meet the maritime sector needs.

The scope of this work is to map and assess the availability, quality, and geographic distribution of various bio-CO₂ streams across Europe, focusing on their potential use as feedstock for RFNBO methanol synthesis. The study examines bio-CO₂ streams from sectors including biogas, biomass power generation, pulp and paper, bioethanol, and the food and beverage industry to evaluate their suitability for methanol production. It provides an overview of key biomass conversion technologies that emit CO₂ as a by-product, together with an overview of CO₂ capture, storage, and transportation technologies. In addition, the study analyzes potential impurities in bio-CO₂ streams and the gas cleaning requirements

necessary to ensure compatibility with methanol synthesis processes. Bio-CO₂ sources are categorized based on parameters such as the CO₂ concentration total emissions, geographic distribution, seasonality, and current CO₂-utilization practices. Through this analysis, the study delivers a harmonized assessment of the opportunities and challenges associated with using bio-CO₂ from RFNBO methanol production. Furthermore, a critical evaluation of technical feasibility and infrastructure readiness is conducted to assess the scalability of e-methanol production in the EU, with particular emphasis on renewable feedstock availability, the hydrogen supply, and supply-chain constraints. A comparison between the current and future bio-CO₂ and green hydrogen availability and projected methanol demand is also performed, including a country-level analysis of emissions, hydrogen capacity targets, and the status of methanol storage and bunkering infrastructure at European ports. Finally, the study presents the conclusions, limitations, and future research needs, offering insights into optimizing the use of bio-CO₂ for sustainable RFNBO methanol production. An overview of the study framework and analytical approach is provided in Figure 2.

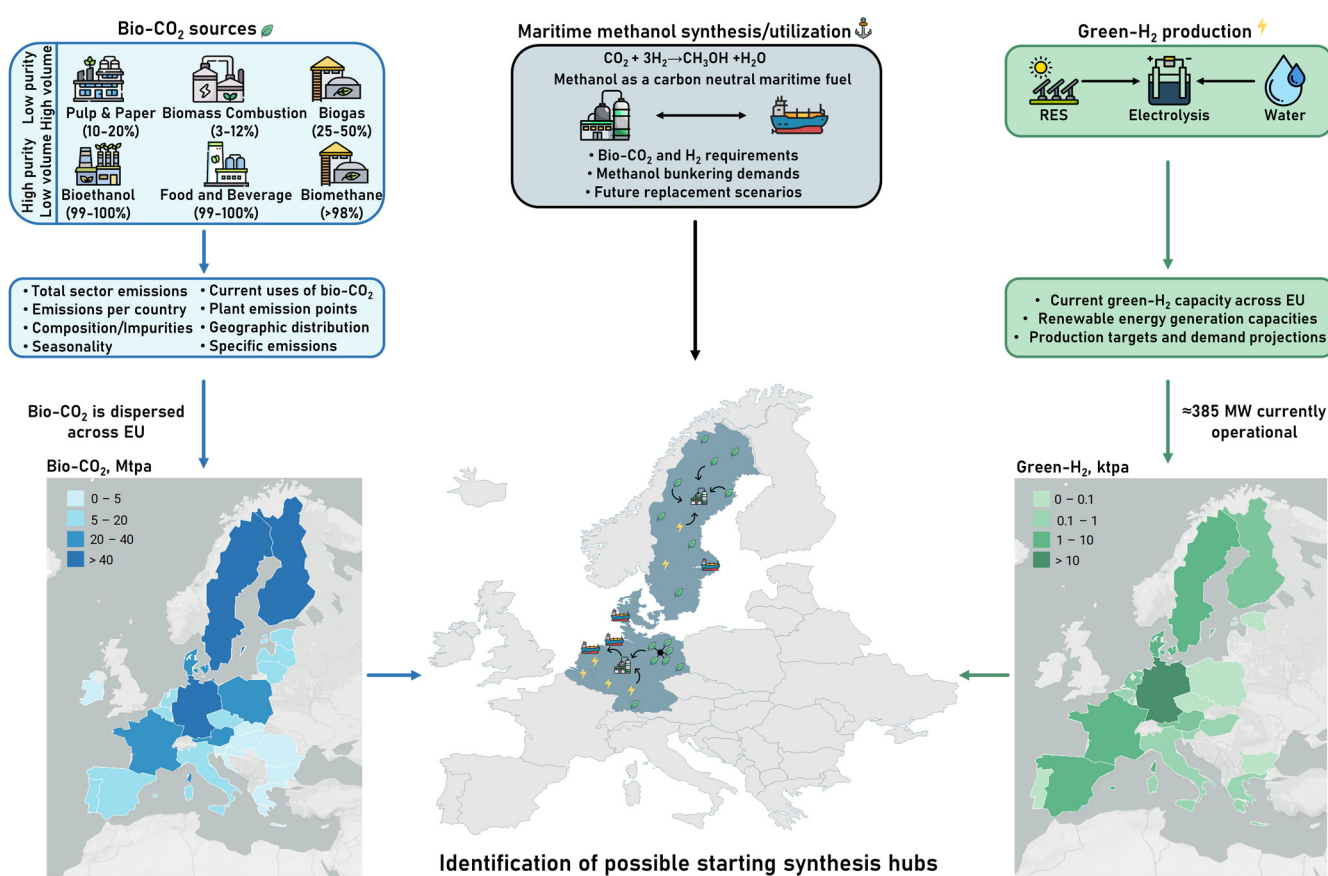


Figure 2. Overview of the study framework, including the key bio-CO₂ sources, evaluation criteria, hydrogen requirements, and infrastructure considerations assessed in this work.

2. Overview of Bio-CO₂ Technologies and Considerations

2.1. Biomass Conversion Processes

The production of bio-CO₂ is the direct result of a variety of biomass conversion technologies. Within the investigated sectors of this work, bio-CO₂ and the related biogenic carbon emissions are not the main product of interest but rather a by-product that mostly remains unexploited and presents an environmental burden. The main biomass conversion processes that generate bio-CO₂ can be summarized into three major categories: combustion, digestion, and fermentation.

Biomass combustion involves the utilization of biomass for the production of heat, electricity, or combined heat and power (CHP). It is a versatile solution with various applications, ranging from domestic heating and district heating to large-scale power generation. In domestic heating, traditional methods such as open fireplaces are being replaced by advanced systems with improved efficiency and reduced emissions [16]. District heating and CHP systems fueled by biomass are widely deployed in Scandinavia and Austria, with increasing scales and efficiencies over time [17]. Larger-scale biomass combustion for electricity production is common worldwide, especially in sectors like the paper and pulp industry, where technologies like fluidized bed combustion are utilized [18]. In the previous years before the lignite phase-out policies, the co-combustion of biomass with coal in existing power plants also gained interest as a cost-effective and environmentally friendlier option for reducing GHG emissions [19]. The associated bio-CO₂ streams, due to the combustion process, will typically have low CO₂ content (<15 vol. %), with high levels of inert gases (mainly nitrogen), oxygen from incomplete combustion, and NO_x, SO_x, and other trace compounds that are inherent to both the combustion process and the biomass feedstock [20]. Apart from the power plants sector, the biomass combustion process is also an important emission point in the pulp and paper industry.

Biomass digestion, or anaerobic digestion, is a biochemical process that decomposes organic materials, such as biomass, organic or domestic waste, manures, and sludges, without the presence of oxygen. This process generates biogas and a nutrient-rich digestate and typically occurs in a sealed container called an anaerobic digester, where microorganisms decompose organic matter [16,21]. The digestion process is, among others, suited for biomass feedstocks with high water contents. This process is well developed and mature, with industrial-scale biogas and anaerobic digestion facilities, as well as landfills, in Europe and worldwide [22]. Through digestion, substantial amounts of bio-CO₂ are produced, which often remain unutilized. Especially in plants that integrate biogas upgrading, where methane is the primary product of interest, the carbon dioxide is typically released into the atmosphere.

Biomass fermentation is a biochemical process in which microorganisms break down organic materials, such as sugars or starches, to produce various useful products, including bio-ethanol [23]. The fermentation process involves pretreatment to break down the biomass structure, followed by hydrolysis to produce sugars that can be fermented into ethanol [24]. The fermentation process is widely applied in the bio-ethanol industry, as well as in the food and beverage industry, to produce wine, beer, etc. [24]. The generated bio-CO₂ from this process is very pure (>99 vol.%), making it relatively feasible to capture and reuse [25]. Generally, because of its high purity, this bio-CO₂ is often reused within the same industry or sold to other food and beverage industries. However, the total bio-CO₂ emissions from this sector account for a smaller percentage of the overall EU bio-CO₂ emissions.

2.2. CO₂ Capture, Storage, and Transportation

Before implementing carbon capture and utilization (CCU) in a specific bio-CO₂ sector, it is crucial to assess the availability of substantial bio-CO₂ volumes and the specific emissions per plant. Essentially, for the same amount of total CO₂ emissions, it is more advantageous to have concentrated CO₂ emissions from a smaller number of point sources/plants rather than a larger number of plants emitting lower levels of CO₂ per plant [14,26]. This approach would help minimize the enhanced capital expenses associated with capture, storage, and transportation, along with their integration with methanol synthesis and water electrolysis units. For example, pulp and paper plants emit large quantities of biogenic CO₂ per facility, but its concentration is diluted as it contains inert components

such as nitrogen that reduce the partial pressure of CO₂ [27]. Alternatively, bio-CO₂ can be separated and stored in highly concentrated streams, such as after biogas upgrading or in the FAB industry, but the total emissions are distributed across installations with lower CO₂ production per plant, making it challenging to achieve economies of scale. This also impacts logistics since biogas plants are typically in rural areas, while the CO₂ end-user facilities, methanol-synthesis plants, and/or hydrogen production units may be located elsewhere, resulting in additional transportation costs. Another important consideration is that not all CO₂ emissions can be effectively captured from the streams depending on the plant size and the fraction of CO₂ in the flue gases; it is anticipated that capture rates could be up to 90% [6].

2.2.1. CO₂ Separation and Capture Technologies

Three main methods of CO₂ capture can be used to reduce CO₂ emissions (especially focused on bio-energy production): pre-combustion capture, post-combustion capture, and oxy-fuel combustion [28,29]. In the pre-combustion separation method, the fuel undergoes pretreatment and, through gasification or reforming, syngas is generated. The mixture of CO and H₂ then undergoes the water gas shift reaction with steam, converting CO to CO₂, which is subsequently separated in the capture subsystem [30]. The higher concentration of CO₂ in syngas makes CO₂ capture less costly for pre-combustion compared to post-combustion capture [28]. In the post-combustion process, CO₂ is captured from the exhaust gas of power plants after combustion. Conventional power plants use air for combustion, producing flue gas at atmospheric pressure with typically less than a 15% concentration. Consequently, the energy penalty and associated costs for the capture unit are higher for the post-combustion process, despite its higher thermal efficiency for electricity conversion compared to pre-combustion [28,29,31]. Oxy-fuel combustion presents a promising technology for CO₂ capture from fuel gas or to modify the combustion process to produce flue gas with a high CO₂ concentration for easier separation. In this method, fuel is combusted in a chamber in an environment of pure oxygen (from an air separation unit) mixed with recycled flue gas. By-product oxygen from electrolysis could also provide a potential high-purity solution for that purpose [32]. The flue gas stream from this system consists mainly of CO₂ and water vapor, with water easily removed via condensation and the remaining CO₂ purified at a relatively low cost [28].

For the three capture methods, several CO₂ separation technologies can be deployed, demonstrating a diversity of technical approaches and materials needed for each method [28,29]. The choice of technology depends on the desired purity of the product and the characteristics of the stream being processed, such as the CO₂ pressure, temperature, concentration, and presence and concentration of trace species or impurities [29,33]. The specific cost of capture is closely linked to the concentration of CO₂ in the stream, the presence of impurities, and the capture efficiency. In certain cases, such as in biomethane plants, CO₂ capture/separation techniques are already integrated within the plant boundaries, thereby avoiding the need for the additional deployment of processes that could potentially increase the cost of the carbon feedstock and consequently the cost of the produced methanol.

2.2.2. CO₂ Storage and Availability

There are various scenarios for the storage of CO₂-containing industrial off-gases [34]:

Off-gases from the process are stored on-site in gas holders. A part of these gases may be employed within the plant (such as for power generation), while the remainder can be utilized for methanol synthesis. However, it is crucial to purify the off-gas stream of any contaminants that could impair the catalyst used in methanol synthesis. CO₂ is extracted

from the off-gases (using methods like amine- or membrane-based processes) or is already available within the plant boundaries (such as in biomethane plants) and then stored in a relatively pure form. Some contaminants are removed from the stream, but additional provisions for gas cleaning are necessary. The adoption of such processes could raise the operating and capital costs, consequently increasing methanol production expenses.

Interim storage of CO₂ might also be necessary during transportation from the source to the final destination. This becomes particularly relevant when CO₂ is transported in liquid form via trucks/ships. Interim storage serves to balance the continuous recovery/offtake of CO₂ from capture or utilization plants between individual truck or ship loads. The required capacity for interim storage will largely depend on the cycle time of the tanker trucks or ships and the desired buffer capacity. However, for pipeline transport from the capture plant to the final destination, interim storage of CO₂ is typically unnecessary [35].

2.2.3. CO₂ Logistics and Transportation

Carbon dioxide can be transported in various states: gaseous, liquid, dense, or supercritical. Multiple studies indicate that gaseous transport is the least energy- and cost-efficient among the four states due to its lower volumetric density. Consequently, CO₂ is usually transported as a liquid for shipping, trucking, or rail transport and as a supercritical or a dense-phase fluid for pipeline transport [36]. For transporting large volumes (>1 Mtpa), only pipeline and maritime transport are considered feasible options. Road transport is generally employed for smaller volumes and shorter distances, especially when constructing a pipeline is not feasible [35,37,38]. Supercritical CO₂ has the properties of both liquid and gas; it has a density similar to a liquid but a viscosity and diffusivity close to that of a gas. Liquid CO₂ transport takes place below the critical point and above the triple point, typically within a temperature range of −56.6 °C to −31 °C and a pressure range of 5.2 to 73.8 bar [35]. The selection of transportation states and methods will, among other factors, be influenced by the volumes being transported, associated costs, location, geographical features, and specific use scenarios.

- Pipelines: CO₂ is transported via pipelines either in a dense phase below the critical temperature or as a supercritical fluid above the critical temperature to prevent phase changes. A crucial aspect of CO₂ pipeline transportation is achieving a high density, indicating a greater mass of CO₂ within a given volume [35,37,38].
- Ships: CO₂ is transported by ships in its liquid phase, which is more cost-effective and efficient compared to gas transport. However, stringent safety measures must be observed, including appropriate wall thickness and operational conditions to prevent phase changes. Common transport conditions involve liquid CO₂ at pressures of 15–18 bar and temperatures ranging from −25 °C to −30 °C, which have become the industry standard for supplying industrial-grade liquid CO₂ [35,37,38].
- Road: Liquid CO₂ is frequently transported by tanker trucks from distribution hubs to industrial consumers. Standard CO₂ semi-trailers with capacities up to 25–30 m³ are available from various suppliers. These trucks operate at pressures of 15–18 bar and temperatures between −25 °C and −30 °C, maintaining a density of approximately 1070 kg/m³. Insulation is employed to keep the CO₂ cool during transportation, although trucks typically lack gasification units. Loading/unloading bays equipped with CO₂ transferring equipment are necessary at receiving terminals. Standard terminals for truck loading/unloading are commercially accessible, making CO₂ road transport comparable to transporting other liquid fuels or pressurized gases [35].
- Rail: While the rail transport of CO₂ is technically feasible, it remains limited, with cryogenic rail cars occasionally utilized for distributing liquid CO₂ to industrial users in certain regions [35].

2.3. Potential Impurities and Gas Cleaning

To examine the potential impurities that are included in the bio-CO₂ feedstock, it is essential to examine the different biomass feedstocks that were initially used in the upstream processes. Impurities and components present in the biomass feedstock may also be found in trace amounts and various forms or compounds in the off-gases of these processes, also necessitating a dedicated gas cleaning process [39]. For instance, biomass with high sulfur contents (such as animal manure) will result in end-products and off-gases that could contain sulfur species such as H₂S, COS, and organic compounds [26,40,41]. Due to the diversity/complexity of the different involved upstream processes and industries, as well as the individual characteristics of each plant, it is difficult to predict beforehand that a particular impurity will be also present in the bio-CO₂ feedstock that will be eventually used for MeOH synthesis [39]. Furthermore, a range of compounds could also be simultaneously removed during the employed CO₂ capture processes resulting in a stream with lower impurities compared to the initial stream. The remaining of this section presents a brief overview of potential contained impurities in the streams, their effects, and potential removal processes.

2.3.1. Water and Moisture

Water contents and moisture may be present in the bio-CO₂ streams that can be used as feedstock for methanol synthesis. The contained water could accelerate the crystallization of Cu and ZnO particles of the MeOH catalysts leading to surface and copper area reduction and thus catalyst deactivation [42]. Furthermore, the product, water, can hinder the thermodynamics of the synthesis reaction, shifting the conversion towards the reactant's side. To this end, water removal and condensation are critical before MeOH synthesis. For multi-reactor synthesis concepts, intermediate water condensation can be conducted to remove the formed water in liquid form and thus further promote the methanol synthesis reaction [43].

2.3.2. Sulfur-Containing Species

Various sulfur-containing compounds, such as H₂S and COS, may be found in the bio-CO₂ stream, posing a threat to metal surfaces through erosion, as well as to the synthesis catalyst. Additionally, SO₂ and organic sulfur compounds could be present, necessitating further gas purification processes before utilization. This is essential to protect synthesis catalysts from deactivation or poisoning and to prevent the formation of unwanted by-products [44]. Regarding sulfur-containing compounds, H₂S is more easily eliminated at ppb levels compared to other sulfur species. Converting COS and organic sulfur compounds to H₂S is a common practice, followed by deep removal through adsorption technology [45]. While acid gas removal methods like SelexolTM or RectisolTM could be employed, they could physically absorb CO₂, which is the main feedstock for the synthesis [44]. Organic sulfur compounds and COS are transformed to H₂S in the hydrodesulphurization reactor by adding hydrogen, with common catalysts being Cobalt and Nickel-based [46]. A sorption bed containing metal oxides like CaO and ZnO can also be utilized to eliminate H₂S, with ZnO converting H₂S to ZnS [47]. Studies have demonstrated that using the ZnO approach, H₂S may be successfully eliminated at ppb levels [47,48]. Due to the potential presence of CO and CO₂ in the bio-CO₂ stream, additional reactions may also take place, reducing the effectiveness of H₂S removal [49].

2.3.3. Nitrogen Species and Ammonia

Typical impurities in bio-CO₂ sources could also include nitrogen compounds like ammonia or hydrogen cyanide. High process temperatures can promote the formation of

nitrogen oxides (NO_x), which are particularly prevalent in biomass combustion processes and need to be eliminated from the exhaust gases [20]. Conversely, ammonia (NH_3) can adsorb onto catalyst sites, leading to decreased catalyst activity at lower temperatures [50]. In addition, it could lead to the formation of additional NO_x during combustion, besides being toxic and corrosive to equipment [51]. Water scrubbers could be deployed to effectively remove ammonia from bio- CO_2 streams such as biogas for instance [52].

2.3.4. Halides (HCl, HBr, HF)

Other compounds present in industrial off-gases include halides such as HCl, HF, and HBr, which can cause corrosion and catalyst poisoning. Experimental findings indicate that HCl can lead to prolonged loss of the catalyst's active surface and promote the sintering of copper crystallites [53]. There is also a risk of forming toxic by-products like polyhalogenated dioxins and furans [54]. Moreover, reactions between HCl and other contaminants, could lead to the formation of NH_4Cl and NaCl , potentially causing issues in downstream pipelines and equipment [55,56]. A common method for removing halides is to use inexpensive sorption materials like NaHCO_3 , which convert HCl into NaCl , while also generating H_2O and CO_2 [50].

2.3.5. Siloxanes

Siloxanes are organosilicon compounds of the form R_2SiO , where R is a hydrogen atom or a hydrocarbon group. Siloxanes are a particular issue especially for biogas plants since they are responsible for the fouling of emission control systems, as well as for the lifespan decrease of the used equipment [51]. Siloxanes could form microcrystalline silicon dioxide (SiO_2) and deposit on valves and cylinder walls, causing abrasion and the blockage of equipment [54]. The primary methods for siloxane removal are water scrubbing or scrubbing using hot sulfuric acid [57]. Additional methods include, among others, adsorption, absorption, refrigeration/condensation, and membrane processes [54].

2.3.6. Oxygen

Due to the nature of combustion processes, as well as the biomass feedstock composition, oxygen might be present at varying composition levels at the exhaust/off-gases. Furthermore, if hydrogen from electrolysis is used, oxygen contents may also be present in the hydrogen stream due to oxygen cross-over or the mixing of oxygen/hydrogen-saturated electrolytes; a O_2 range of 0.2–0.6% in hydrogen is expected for alkaline systems [58]. In general, O_2 could lower MeOH catalyst activity/selectivity and conversion rates, leading to irreversible poisoning effects and should be removed prior to the reaction [59]. Oxygen is also the main oxidizing agent and can cause corrosion in steel pipelines leading to critical safety and operational consequences [60]. Oxygen traces in hydrogen streams could be removed using a catalytic recombination with hydrogen, producing water and heat (exothermic reaction) [58]. For the treatment of off-gases, catalytic oxidation with hydrocarbons such as methane, which is included in biogas streams, can be applied [61]. Since this removal step, apart from heat, produces water, it can be usually applied before a water-removal/drying step [58].

2.3.7. Trace Elements and Heavy Metals

Due to the variety of feedstocks, the CO_2 may also contain trace elements and heavy metals. Trace elements such as Zn and Pb may cause corrosion problems, while others such as Hg, Cd, Pb, and Cr are also hazardous to human health and the environment. The following criteria determine the trace element form and if it appears in the gas or particulate phase [62]: temperature and pressure, trace element resistance in the incoming material,

oxidizing or reducing conditions, presence of halogens (like chlorine), and presence of compounds acting as sorbents (such as Ca).

Table 1 summarizes the main impurities per biogenic-CO₂-emitting sector. Biomass combustion and pulp and paper plants exhibit the highest impurity levels, indicating increased conditioning requirements and associated costs. Further details are provided in Section 4. In addition, Table 2 presents numerical catalyst-tolerance limits for the most common impurities, focusing on species whose deactivation mechanisms have been extensively studied. Currently there are no numerically defined regulatory limits for siloxanes as poisons of methanol synthesis catalysts; the existing literature generally states only that siloxane contaminants must be removed to prevent irreversible catalyst deactivation.

Table 1. Non-exhaustive overview of potential impurity ranges per sector.

Sector	CO ₂ Concentration (vol. %)	Potential Impurities Range	Ref.
Biomass power plant	3–15%	1.6–2.8 mol% (CO); 3–4.1 mol% (H ₂); ≈15 mol% (H ₂ O); ≈3 mol% (O ₂); ≈68 mol% (N ₂); 10.3–65.3 ppmv (NO _x); ≈16 ppmv (SO _x); 4–6 ppmv (HCl); ≈3 ppmv (NH ₃)	[63–65]
Pulp and Paper	13–14% (Recovery boiler)	Recovery boiler 56.1–67.6 mol% (N ₂); 2.3–5.5 mol% (O ₂); 17–24.3 mol%	[65,66]
	20–23% (Lime Kiln) 11–12% (Power boiler)	Lime Kiln 29.9–47.4 mol% (N ₂); 1.2–5.5 mol% (O ₂); 30.9–41.2 mol% (H ₂ O); 9–50 ppm (SO _x); 175–442 ppm (NO _x); <15 ppm (H ₂ S); 20–30 ppm (Particulates)	
Biogas	20–50%	Power boiler 53.4–59 mol% (N ₂); 1.7–8 mol% (O ₂); 20.5–32.7 mol% (H ₂ O); <40 ppm (SO _x); 84–150 ppm (NO _x); <15 ppm (H ₂ S); 120–150 ppm (Particulates) 0–7000 ppm (H ₂ S); 1–5 mol% (H ₂ O); <0–6 mol% (N ₂); <0–1.6 mol% (O ₂); 70–140 ppm (NH ₃); <0.01–0.25 mg/m ³ (Halogens); <0.03–15 mg/m ³ (Siloxanes); 0–200 mg/m ³ (Aromatic); 0.1–1.3 mg/m ³ (Benzene); 0.2–11.8 mg/m ³ (Toluene)	[51,67,68]
Bioethanol	97–100%	0–3 mol% (H ₂ O)	[69]
FAB	99–100%	Traces of H ₂ S, H ₂ O	[69]

Table 2. Catalyst limits for major impurities and potential conditioning technologies.

Component	Limit	Conditioning	Ref
Sulfur compounds	<0.05 ppmv	Wet chemical scrubbing using alkaline or chelated iron solutions	[70]
Halogens	<0.05 ppmv	Wet absorption with alkaline solutions	[67,71]
Heavy metals	<5 ppb	Guard beds	[72,73]
PM	<0.1 mg/Nm ³	Cyclones, bag filters, electrostatic precipitators, and wet scrubbers	[74,75]
Alkali	<0.01 ppmv	Guard beds	[73,74]
NH ₃	<0.05 ppmv	Guard beds	[73,76]

3. Methodology

To categorize and map the different bio-CO₂ sectors, the following aspects, which are directly linked to the suitability of these streams for methanol synthesis, are evaluated:

- Total sector emissions: The cumulative emissions of each bio-CO₂ sector and its contribution to the overall emissions offers an initial indication of the sectors that predominantly contribute to EU bio-CO₂ emissions and therefore their potential for methanol synthesis.
- Bio-CO₂ stream concentration (%): This aspect pertains to the CO₂ content in the total bio-CO₂ streams, which, among other factors, depends on the type of upstream process and the composition of the feedstock. A higher CO₂ concentration indicates that more

CO₂ can be utilized, as well as lower costs per captured CO₂ (if the application of capture techniques is required).

- Seasonality (if any): Certain bio-processes emit bio-CO₂ within a certain period in a year and utilize a variety of biomass feedstocks. This means that their operation could be directly influenced by seasonality, with emissions showing peaks at certain times of the year/months, depending on the industry and the operation mode [77]. For example, wine facility operation is directly related to the grape harvest season, which in most regions is conducted in late summer [78]. Other sectors, such as biomass combustion coupled with district heating are directly linked to the heating requirements of each location and exhibit increased operation from September/October until April/May. Seasonality is also an important factor for biomass logistics, especially for agricultural residues where it can further add costs to the total production [17,79].
- Potential impurities and other compounds: Potential impurities and other compounds present in the bio-CO₂ stream could impact the methanol synthesis catalysts and associated plant equipment. The presence of these impurities will also determine the necessary gas cleaning processes before the stream can be transported and utilized for synthesis.
- Current uses of the bio-CO₂ stream: Already established uses of bio-CO₂ streams indicate a lower possibility for utilization in methanol synthesis, whereas no utilization (or atmosphere release) indicates the need for the application of capture and storage techniques that could increase production costs.
- Bio-CO₂ emissions points in the plant: Bio-CO₂ can be generated at multiple locations within a specific plant. This study will identify various generation points within these plants, with a primary focus on the most viable points for capture and utilization.
- Geographic distribution and emissions per plant: The various bio-CO₂ emitters may be geographically distributed across different locations, with a key factor being the CO₂ emissions per plant. Higher total sector emissions combined with lower emissions per plant suggest a decentralized sector, presenting challenges in achieving substantial cost reductions through economies of scale. This aspect will also impact the logistics of transporting CO₂, H₂, and methanol and in turn affect the overall cost of methanol production.

4. Analysis of Bio-CO₂ Sectors

Based on the described methodology and aspects described above, this section provides more information on the biogas (Section 4.1), biomass combustion (Section 4.2), pulp and paper (Section 4.3), bioethanol (Section 4.4), and food and beverage sectors (Section 4.5). For comparison purposes, the option of direct air capture is also outlined as an alternative potential source of CO₂ for methanol synthesis (Section 4.6).

4.1. Biogas Plants

Biogas is generated through the microbial decomposition of biomass in anaerobic conditions, a process known as anaerobic digestion (Section 2.1). The primary components of biogas are methane and carbon dioxide, hydrogen sulfide, and trace amounts of hydrogen, nitrogen, and oxygen [80,81]. Diverse organic materials, including crops, agricultural waste, manure, biowaste, and sewage sludge, could serve as feedstocks for biogas production plants. These substrates undergo anaerobic digestion within the plant boundaries, where a series of bacteria decompose the organic material, releasing a mixture of gases. The composition of biogas varies depending on the type of feedstock used; typically, it contains 50–80% methane and 20–50% carbon dioxide [67,68,82]. According to the European Biogas Association (EBA) and other sources [83,84], the most common used feedstock for biogas

production in Europe, at around 42%, is based on crops. The second most used feedstock is agricultural waste and has a significantly lower gas formation rate, therefore contributing to less than 24% to the total biogas production [82].

Biogas is a feedstock that after treatment can be used in diverse applications including for the production of electricity/heat, injection into the gas grid, vehicle fuel, and production of chemicals. To prepare biogas for these applications, a series of gas cleaning/conditioning technologies are required, including cooling, draining, drying, and cleaning, to remove H₂S due to its corrosive effect. The obtained gas can be either applied directly for the production of electricity and heat or upgraded to biomethane (98% CH₄) [83]. Currently, approximately 75% of biogas plants in the EU utilize biogas for combined heat and power production [57]. Figure 3 shows the concentration of biomethane plants in the EU according to the Joint Research Center (JRC) database [85].

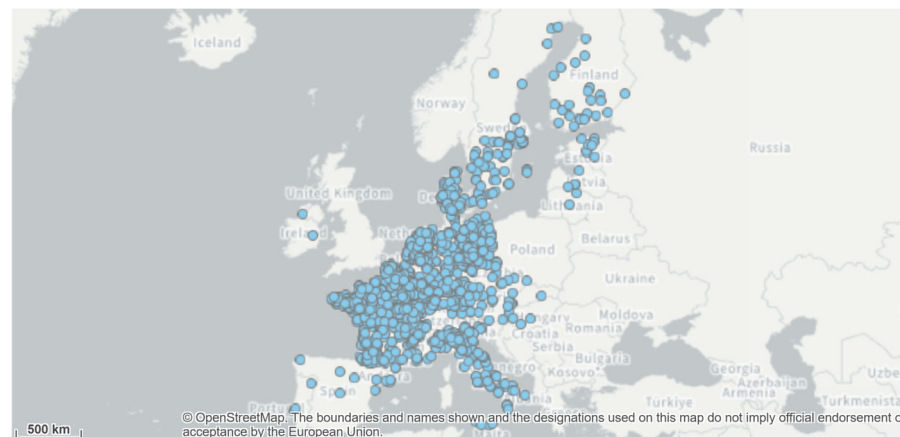


Figure 3. A snapshot of EU biomethane industries.

The concentration and the quality of the impurities detected in the biogas off-stream are strongly connected to the feedstock of the anaerobic digester (as well as the upstream process). Table 3 presents a range of the biogas composition and impurities referring to diverse utilized feedstocks.

Table 3. Biogas components and impurities for different feedstocks [26,51,86].

Feedstock Type	N/A	Agricultural Waste	Landfills	Industrial Waste	Sewage Treatment
		Main components (vol. %)			
Methane (CH ₄)	50–70	50–80	50–80	50–70	60–65
Carbon dioxide (CO ₂)	30–50	30–50	20–50	30–50	35–40
Nitrogen gas (N ₂)	0–3	0–1	0–3	0–1	1–2
Oxygen (O ₂)	0.0–0.5	0–1	0–1	0–1	0.05–0.7
Hydrogen (H ₂)	0.0–1.5	0–2	0–5	0–2	-
Water vapor (H ₂ O)	1–7	-	-	-	-
Carbon monoxide (CO)	0–1	0–1	0–1	0–1	-
		Trace components (ppm)			
Ammonia (NH ₃)	0–308	traces	traces	traces	1–7
Hydrogen sulfide (H ₂ S)	20–850	0.7	0.1	0.8	0.5–6800
Terpenes	0–500	-	-	-	-
BTX (Benzene, Toluene, Xylene)	0–7	-	-	-	-
Hydrocyanic acid (HCN)	0–0.003	-	-	-	-
Fluorine compounds (R-F, incl. HF)	0–1.3	-	-	-	-
Chlorine compounds (R-Cl, incl. HCl)	0.1–5	-	-	-	-
Siloxanes (D4 & D5)	0–3.4	-	-	-	1–400 *
Halogens	-	-	-	-	0–2 *

* Values in mg/m³.

According to the EBA, there are around 20,000 biogas plants operating in Europe. Around 1322 (2023 data) of those upgrade and inject biomethane into the natural gas

grid, and around 18,943 (2021 data) units use biogas for CHP production [34,87]. The combined biogas and biomethane production was approximately 22 bcm in 2023, of which 4.9 bcm is upgraded to biomethane [88]. Biogenic CO₂ emissions from anaerobic digestion were adopted from [89], which derives process-related emissions using energy production data reported in the EBA 2023 statistical report [90]. In that study, national-level biogas and biomethane production reported by the EBA are converted into CO₂ emissions using assumptions on the biogas composition, heating values, and conversion efficiencies. The total estimated biogenic CO₂ emissions from anaerobic digestion in 2023 amount to 41.3 Mt, while another source reported approximately 23 Mt from biogas production in 2017 [25]. These values reflect emissions occurring during the digestion process and exclude the upstream feedstock supply and downstream utilization.

Another potential source of biogas (and of bio-CO₂) is the utilization of landfills. In landfills, municipal solid waste (MSW) is deposited underground where it undergoes an aerobic (with oxygen) decomposition stage producing methane along with carbon dioxide and other components in smaller concentrations. The resulting mixture, also called landfill gas (LFG), has a similar composition of biogas with some key differences. LFG is characterized by a lower methane content (45–55%), higher nitrogen concentrations (5–15%), and carbon dioxide around 30–40%. In addition, it contains higher amounts of impurities such as oxygen, water vapor, sulfur, and hundreds of other contaminants. These variations in compositions influence its energy potential and the technical requirements for its purification and utilization [91]. Due to the uncontrolled nature of LFG production and the need for extensive purification, it is not an optimal choice for sourcing renewable carbon for methanol production compared to the more controlled biogas generation processes in biogas plants [92].

Biogas plants present a large geographical distribution, mainly located in the countryside and away from urban centers due to logistics and odor issues, with small amounts of CO₂ emissions per plant. Biogas upgrading is a process for recovering the contained methane, which can be further utilized in other applications [93]. Various techniques for biogas upgrading are available to minimize the presence of CO₂, H₂S, and other contaminants in the desired output, thereby enhancing the methane content [94,95]. The main biogas upgrading processes are as follows: water scrubbing, membrane technologies, biological methods, chemical/physical absorption, pressure swing adsorption, in situ methane enrichment, hydrate formation, and cryogenic separation [96,97].

As the primary objective of biogas upgrading is to isolate and refine the methane content within the biogas, minor compounds are frequently eliminated to a certain extent alongside the CO₂ stream. However, the CO₂ stream, often characterized by high concentrations, typically exceeding 98%, may still contain significant amounts of impurities and is unsuitable for most utilization applications for chemical synthesis without further treatment [26]. In general, most of the employed upgrading processes are effective and capable of recovering up to 97% of the methane present in biogas. The yield of biomethane production and the composition of impurities in the CO₂ stream are dependent on the organic feedstock utilized [82].

Within the biogas plant boundaries, biogenic CO₂ could be generated through the decomposition, digestion, or combustion of biomass or biomass-derived products [87]. The various CO₂ generation points within a biogas plant are primarily three, with the most suitable for MeOH synthesis being the CO₂ after biogas upgrading:

- During the biogas upgrading process, biogas undergoes separation into methane and carbon dioxide to recover biomethane, which can be used in the same manner as natural gas/methane but with a higher environmental efficiency. The relatively high purity of CO₂ renders its capture cost-effective, and, in many plants, the biomethane

separation unit is already included within the plant boundaries, thus reducing the required additional capital investments. This method stands out as the primary opportunity for capturing and reusing CO₂ since the majority of plants aim to upgrade/recover methane from the raw biogas stream, which can be further stored and used for MeOH synthesis [97].

- In biogas plants equipped with CHP systems, biogenic CO₂ is generated from the flue gas emitted during the combustion of biogas. However, this exhaust stream contains a significant proportion of inert components such as nitrogen, as it involves post-combustion capture, resulting in low CO₂ concentrations (<15%) [26,87].
- Another potential route for capturing biogenic CO₂ is through the production of bio-hydrogen from raw biogas. This process entails specialized methods utilizing biogas and accounts for only a minuscule percentage of the overall emissions in a biogas plant [98,99].

The biogas upgrading process is currently the most accessible source of concentrated biogenic CO₂. This biogenic CO₂ is “ready-to-use” (or at least after conditioning) and in many cases is released into the atmosphere [34,87]. The upgrading of biogas to biomethane is already included in several plants, which is also in line with the current trend of biomethane injection into natural gas pipelines and therefore presents a bio-CO₂-utilization option with lower demands and investment needs for CO₂ capture and conditioning.

Typically, this bio-CO₂ is emitted into the atmosphere. Modern facilities, however, are aiming to generate biomethane and often integrate a segment for storing and using CO₂ within the plant premises [22]. Beyond its application in the food and chemicals industry [6], CO₂ is also investigated for the production of additional methane through the addition of renewable hydrogen [100]. This aspect is also in line with the current trend in the biogas sector, where biogas facilities can be gradually transformed into biorefineries, with diverse types of products. Key features of biorefineries include multifunctional concepts with high levels of process integration and the use of diverse bio-based raw materials, preferably non-food materials [101]. In addition, studies have been published estimating and evaluating methanol production using renewable hydrogen and biogenic CO₂, derived from biogas plants, which was captured and utilized after biogas upgrading [97,102].

The seasonality of biogas plants is directly related to the used feedstock. For instance, biogas plants co-located with animal farms are not expected to experience large fluctuations throughout the year regarding their operation. For other biogas plants that use food waste, their availability, as well as composition, can vary considerably depending on the season [103]. Agricultural residues such as corn stalks or wheat straw may be more abundant after harvest seasons, leading to increased biogas production during those times. In general, biogas and bio-methane producers are targeted to mitigate these seasonality aspects and achieve relatively constant annual production rates through feedstock flexibility, as well as optimized digester operation and system designs.

4.2. Biomass Power Plants

Biomass power plants convert the chemical energy of organic matter into electricity. A diverse range of biomass materials can be used for power generation, such as wood waste, agricultural residues, animal waste, and energy crops [104]. Biomass combustion is a leading method for bioenergy production, utilized in both small-scale and large-scale systems for generating heat, electricity, or CHP. This technology is commercially well-established, with biomass being used in steam boilers that are linked to steam turbines and power generators. Power generation efficiencies vary based on the biomass type and system size, ranging from 24 to 38% for plants between 10 and 50 MW and 32 to 42% for plants exceeding 50 MW [105]. Despite its advantages, biomass combustion poses

challenges due to the high fraction of alkali, chlorine, heavy metals, and other contaminants present in biomass ash. These elements increase the risk of issues such as Particulate Matter (PM) emissions, fouling, slagging, and the corrosion of boiler heating surfaces [105]. However, flue gases from bioenergy generation contain low CO₂ concentrations, which will eventually increase the respective capture costs [6].

The utilization of biomass pellets, primarily derived from wood, offers the opportunity for both the partial and complete replacement of coal, leading to significant reductions in emissions of NO_x, SO_x, and CO₂. Biomass plants source their materials from local/regional forests, agricultural, or food manufacturing industries. The co-firing of biomass has been effectively implemented in many combustion plants where coal, lignite, peat, or wood residue from the pulp and paper industry serve as the main fuel. Certain biomass fuels have high moisture contents, which can affect plant efficiency; while fuel drying can enhance efficiency, wood chips and bark are often combusted directly without pre-drying, as their moisture content typically falls below 10–15%. Nevertheless, the potential generation of organic emissions, such as wax and aromatic compounds, poses challenges as these substances can adhere to flue-gas channels and create fire risks in electrostatic precipitators, while aromatic compounds may cause odor nuisances for nearby residents [106]. Various combustion technologies are employed for biomass, including grate firing, fluidized bed combustion, and pulverized fuel firing, with the choice depending largely on the boiler size and desired fuel range [20,107]. Waste incineration is also used for the treatment of a wide range of wastes such as municipal and hazardous waste and sewage sludge. Basically, waste incineration is the oxidation of the combustible materials contained in the waste, where waste is generally highly heterogeneous materials, consisting of organic substances, minerals, metals, and water. During incineration, flue gases are produced, which contain the available fuel energy as heat [108,109]. In fully oxidative incineration, the main components of flue gas are vapor water, nitrogen, oxygen, and carbon dioxide. Depending on the material incinerated and the operating conditions, smaller amounts of CO, halides, NO_x SO₂, Volatile Organic Compounds (VOCs), ammonia, and heavy metal compounds are formed [108,109].

The number of large combustion plants in Europe was estimated to be approximately 3400 in 2021 [110]. The same year, 45.6 Mtoe of biomass fuels and bioliquids were used to produce 14.6 Mtoe of gross electricity that made up 15% of the total gross renewable electricity mix and 6% in the total gross electricity, whereas 74% of gross electricity from biomass was produced in combined heat and power plants. Solid biomass is the most used type (54.8%), followed by biogas (31.1%) [111]. Figure 4 presents an overview of combustion plants that are using biomass feedstocks to produce heat and electricity in Europe [112].

Biomass combustion plants illustrate a large distribution in sizes (ranging from small- to large-scale) and consequently with small or large amounts of CO₂ emitted. In general, there is a large variation in the bio-CO₂ estimations from the biomass power plant sector, since in many cases, the calculation methodology and the used data were not transparent and/or there were different feedstocks and processes included in the calculations. In addition, bio-CO₂ emissions from biomass power plants are difficult to estimate since those plants are also co-firing different feedstocks. In this study, the biogenic CO₂ emissions from biomass combustion were estimated using the tier 1 methodology for stationary combustion sources of the 2006 IPCC Guidelines for National Greenhouse Gas Inventories [113], according to the following:

$$Bio - CO_2 = CF_{biomass} \cdot EF_{biomass} \quad (1)$$

where *Bio-CO₂* represents the total biogenic emissions in kg, *CF_{biomass}* is the thermal energy input of solid biomass combusted in TJ, and *EF_{biomass}* is the emission factor for solid

biofuels in kg of CO₂/TJ. The amount of solid biomass combusted was sourced from the Eurostat energy balance dataset, which reports annual electricity and heat generation from primary solid biofuels in energy units (TJ) [114]. Since the energy balances provide energy output, the corresponding biomass fuel input was calculated by assuming an average conversion efficiency of 35% for biomass combustion plants, consistent with literature values [105,115]. For the emission factor, the 2006 IPCC Guidelines suggest a range of 95,000 to 132,000 kg CO₂/TJ from solid biofuels, mainly wood and wood waste [113]. In 2023, EU gross electricity production utilizing primary solid biofuels reached 78.4 TWh (a decrease from the 88.39 TWh recorded in 2022) [114], resulting in 76.7–106.5 Mtpa of bio-CO₂. Furthermore, heat production from primary solid biofuels accounted for an additional 138.73 TWh, contributing approximately 138–191.7 Mtpa. In total, the estimated emissions from biomass power plants for electricity and heat production are estimated at 214.6–298.2 Mtpa and are within the acceptable range in comparison with previous works, which estimated the maximum theoretical amounts of bio-CO₂ available in Europe from the combustion of solid biofuels as 287–437 Mtpa [14,15,25,26]. However, to ensure methodological consistency with comparable sectoral studies [14,25] and to provide a conservative baseline for further analysis, a representative emission factor of 100,000 kg CO₂/TJ was adopted. Utilizing this value, the total biogenic CO₂ emissions for the 27 EU Member States in 2023 from biomass combustion are estimated at 223 Mtpa.

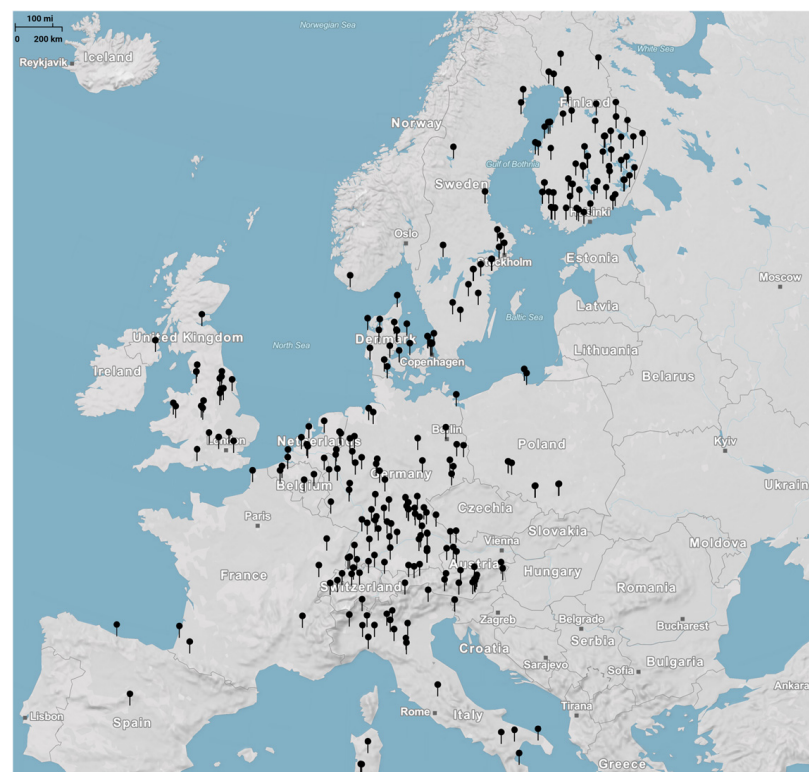


Figure 4. Overview of EU biomass power plants.

The emissions from biomass plants are primarily affected by factors such as the composition of the fuel, the combustion process, and the flue-gas-treatment methods. The key components in flue gases include CO₂, SO₂, NO_x, dust, NH₃, CO, HF, HCl, and Hg. Flue gases from biomass combustion typically contain 3–15% CO₂ [6,14,63]. However, these gases also contain various other components, as mentioned above, rendering the extraction and capture of CO₂ in pure form technically and economically challenging. This technical complexity often translates into higher financial investments, thereby reducing

the economic viability of CO₂ utilization from biomass combustion compared to other industrial sources like the bioethanol and biomethane sector [14].

NO_x emissions are also influenced by combustion characteristics, with higher emissions often requiring NO_x concentrations in the flue gas to be reduced using a DeNO_x system. Grate systems, characterized by low combustion temperatures, are advantageous for controlling NO_x emissions [78,116]. Techniques such as overfire air injection and low excess air are commonly used to minimize NO_x generation. In fluidized bed combustion, NO_x emissions are typically lower than in conventional pulverized fuel combustion. Biomass feedstocks used for combustion generally have low or moderate sulfur contents, leading to low emissions that often do not necessitate desulfurization [116,117]. However, when higher-sulfur-content biomass is used, post-combustion dry injection processes, such as injecting calcium hydroxide or sodium bicarbonate before a bag filter, are employed to reduce SO_x [118]. In grate combustion systems, most of the ash remains on the grate and is collected as bottom ash, with only a small portion exiting as fly ash and being collected in dust-reduction devices. Dust abatement in grate-fired combustion plants involves the use of both Electrostatic Precipitators (ESPs) and bag filters, with bag filters being the more commonly utilized option [20].

In biomass power plants, seasonal variations can impact operations due to changes in the availability and price of certain biomass feedstocks throughout the year. To address these fluctuations, power plants can leverage fuel switching flexibility, allowing them to use a range of locally available bio-feedstocks to maintain electricity production [119–121]. In addition to feedstock seasonality, other seasonal factors are inherent to their operation. For example, while biomass power plants generating electricity may need to operate year-round, biomass district heating plants experience fluctuating heat demands between summer and winter. This variation in demand could impact both their operation and the associated CO₂ emissions [79,122].

As previously mentioned, bio-CO₂ is generated from biomass combustion and can be captured from power production plants or CHP plants. Biogenic CO₂ can be extracted from the combustion flue gas, where the CO₂ concentration is typically estimated to be between 3 and 15% [6,14]. Certain studies have been published the estimation and evaluation of methanol production using biogenic CO₂, derived from biomass plants flue gases [25,123–125].

4.3. Pulp and Paper Plants

Europe ranks as the world's second-largest producer of pulp and paper, contributing to approximately a quarter of the global production [126]. Paper is manufactured from pulp: a soft, moist material primarily composed of cellulose extracted from wood, plants, or recycled paper. Pulp can be produced either through chemical processes or by grinding the raw materials and mixing them with water. The resulting pulp mixture, combined with water and chemicals, is then spread, dried, and cut into sheets and rolls to produce paper [127]. Recycled fibers represent one of the primary feedstocks used in the pulp and paper sector, and the recycling rate of paper in Europe is notably high, reaching 71.4% in 2021 [127]. Recycled fibers constitute roughly half of the raw materials utilized for paper products in Europe. In general, the pulp and paper industry is responsible for approximately 2% of the global industrial CO₂ emissions and over 7% of total European industrial CO₂ emissions [128].

Pulp and paper production occurs in integrated, non-integrated, semi-integrated, or recycled mills. Integrated mills produce both pulp and paper, while non-integrated mills specialize in either pulp or paper production. Pulp is made through mechanical, chemical, or semi-chemical processes, resulting in mechanical pulp or chemical pulp. Mechanical

pulping involves grinding wood with water, while chemical pulping utilizes chemicals to separate lignin from wood chips. Recycled pulp, obtained from de-inked recycled paper, is also used. The papermaking process involves refining pulp fibers, blending them with additives, forming a continuous web, pressing, drying, calendaring for smoothness, and reeling. Additional processes include coating, printing, and finishing for various end-use applications such as newsprint, writing paper, or handmade paper [18,129].

Europe produces about 25.6% of the world's pulp and 26% of the world's paper making [130] with more than 861 mills operating in Europe in 2022, with relatively large amounts of CO₂ emissions per plant. The pulp and paper industry has reduced its carbon emissions by 39% from 2005 and is the largest industrial renewable energy producer and consumer; more than 60% of industry's total primary annual energy consumption is biomass-based. In a similar manner to the bioenergy sector, there is a large variety of estimations for the total biogenic emissions of the pulp and paper sector [6,126,129,131]. Bio-CO₂ emissions resulting from pulp and paper production were sourced from the European Environmental Agency (EEA). The EEA provides a comprehensive dataset that includes location and administrative data for the largest industrial complexes in Europe, along with releases and transfers of regulated substances to various media. It also covers waste transfers reported under the European Pollutant Release and Transfer Register (E-PRTR) [132]. Based on the compiled dataset, total biogenic CO₂ emissions from pulp and paper facilities across the EU's 27 member countries were estimated at approximately 73.9 Mt in 2023, with other sources reporting 68 Mt in 2016 [133] and 92 Mt in 2020 [134]. The Scandinavian pulp and paper industry is estimated to contribute a large percentage to the total European bio-CO₂ emissions [6].

Figure 5 shows the map of the pulp and paper and the timber industries of Europe, which are strongly interlinked. The location of the pulp and paper plants is usually located close to forest and timber industries since wood is the main raw material of this industry. Additional location aspects are related to the water requirements of the plant since they require vast amounts of fresh water, as well as the potential of inexpensive electricity production required for internal processes. To this end and in a similar manner to the rest of the investigated sectors, the location of the pulp and paper plant is a critical parameter that affects the overall planning and value chain of maritime methanol synthesis, requiring additional provision for the transportation costs of bio-CO₂, renewable hydrogen, and/or methanol to the respective production locations/demand centers.

Since the paper-manufacturing process itself generates very low direct emissions, the majority of emissions stem from the use of fossil and non-fossil fuels for steam generation and heating on-site [135]. Chemical pulping processes, especially the Kraft pulping method, are the primary methods for producing pulp. This process generates substantial point source emissions, mainly from the combustion of lignin in the recovery boiler, which is separated from cellulose during pulping. Additional significant emission points include the lime kiln, where lime mud is heated to recover lime, and possibly bark or auxiliary boilers. These boilers can be fueled by various energy sources such as natural gas, coal, oil, or biomass [128]. The recovery boiler is the largest source of CO₂ emissions at a Kraft pulping mill, where concentrated black liquor from pulping is processed, recovering sodium-based pulping chemicals and generating significant amounts of biogenic CO₂ emissions [136,137]. Typically, the CO₂ concentration in the recovery boiler ranges from 10 to 15 vol. % [18,138]. The lime kiln is typically powered by heavy fuel oil or other fossil fuels, leading to CO₂ emissions from both the fuel (fossil CO₂) and the wood raw material used in the pulp mill (biogenic CO₂). Consequently, the CO₂ concentration in the lime kiln is generally high, often around 20 vol. % [18]. Many pulp mills also include an additional power boiler for burning materials such as bark and hog fuel, with typical CO₂ concentrations between

10 and 15 vol. %. The CO₂ concentration in this biomass-fired boiler is comparable to that of the recovery boiler, typically ranging between 10 and 15 vol. % [138,139]. In a similar manner to biomass power combustion plants, most pulp and paper mills operate power plants, auxiliary boilers, steam blocks, or combined heat and power plants on-site to produce the power and heat required for those processes. In consequence, pulp and paper off-gases from the boilers and kilns are expected to contain a diluted content of CO₂, along with inerts and pollutants such as dust, NO_x, SO₂, CO, and H₂S [18].

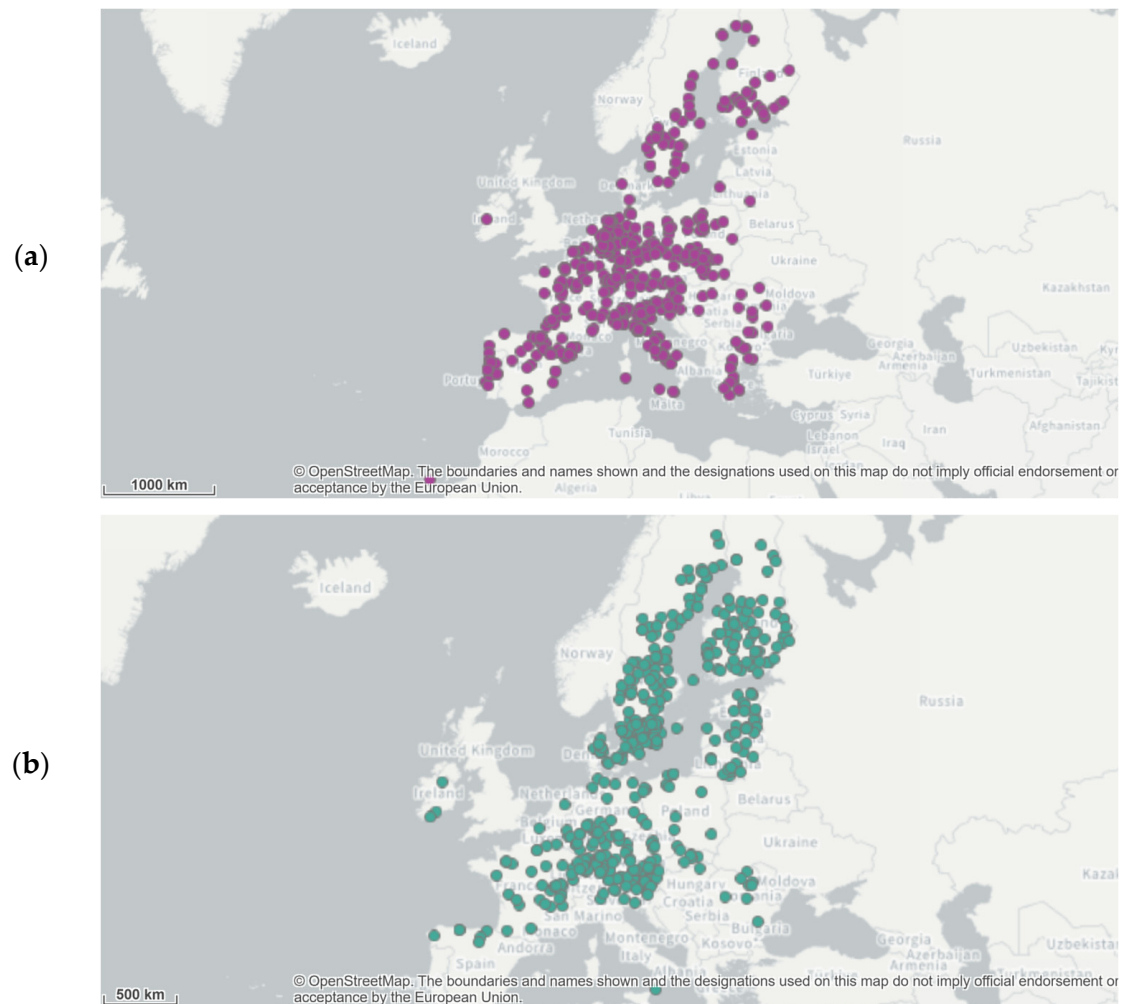


Figure 5. EU (a) pulp and paper and (b) timber industries (data from the JRC [85]).

4.4. Bioethanol Plants

Bioethanol is a liquid biofuel produced through the fermentation of a range of feedstocks, such as corn, soybeans, crops, wheat straw, sugar beet, sugarcane, and woodchips [23,140]. Bioethanol can be used directly in vehicles, operating in a manner similar to conventional fuels. Notably, bioethanol boasts a high-octane rating, allowing for elevated engine compression ratios that enhance engine efficiency and performance with, however, a lower volumetric energy density compared to conventional fuels. It is estimated that approximately 78% of European industrial bioethanol consumption is used as a component of vehicle fuels [26]. Figure 6 shows a map of the sugar and starch industries in Europe, according to the JRC database [85], which are strongly linked to bioethanol and FAB industries.



Figure 6. EU Sugar and starch industry.

The production of bioethanol encompasses three primary processes: pre-treatment to break down hemicellulose and cellulose, hydrolysis of cellulose to obtain fermentable sugars, and fermentation of sugars into ethanol and CO₂, with distillation following to separate and purify the ethanol product [141]. As a rough estimate, around 950 kg of bio-CO₂ is emitted per ton of produced bioethanol [15]. CO₂ released during fermentation is characterized by a very high purity, making it particularly attractive for direct utilization, as it does not require energy-intensive capture or conditioning steps prior to storage, transportation, and methanol synthesis. However, bioethanol-derived CO₂ represents only a small fraction of total CO₂ emissions and is often internally reused within production facilities or sold to other industries, limiting its availability for external utilization. Moreover, it is anticipated that bioethanol production will gradually decline towards 2050 due to the increasing purchase of electric vehicles and reduced demand for biofuels in road transportation, thereby impacting the bio-CO₂-production potential of this sector [142]. This means that bioethanol facilities are expected to play a more important role in short-term deployment and specialized applications rather than as large-scale, long-term CO₂ supply sources.

Globally, the production of ethanol is primarily sourced from maize (60%), sugarcane (25%), wheat (3%), molasses, and residues from other grains such as maize, cassava, or sugar beet (2%). Within the EU, the main feedstocks for bioethanol production include sugar beets (38%), maize (cellulosic) (36%), and wheat (14%), with smaller amounts from triticale, barley, and rye [77].

In 2022, there was a significant increase in the utilization of grains as feedstock for bioethanol production, driven by expanding production and changing feedstock compositions. Despite a decline in the EU grain harvest, increased imports from Ukraine, particularly of wheat, supported the use of grains for bioethanol production. Across France, Germany, Czech Republic, Belgium, and Austria, sugar beets and their derivatives are key feedstocks for bioethanol production. In France, sugar beets are exclusively processed for bioethanol in sugar beet processing plants equipped with on-site ethanol distillation capabilities. In other countries like Austria and Belgium, beet pulp may also serve as feedstock for ethanol production [143].

The EU production of biofuels is approximately 20 billion liters per year, of which 6.4 billion liters was bioethanol in 2023 [77,144]. Biofuels supply was about 6.3% of the total transport fuel consumption in the EU. The majority of bioethanol produced in the EU is made from sugar and starch-based crops, all derived from food-based crops [77]. Most European bioethanol fermentation plants are based in France, followed by Germany and the UK. In total there are around 59 bioethanol plants in Europe [145]. Biogenic CO₂

emissions from bioethanol production were estimated based on the stoichiometry of glucose fermentation, in which 0.75 kg of biogenic CO₂ are released per liter of bioethanol produced, consistent with the theoretical conversion of glucose to ethanol and CO₂ [89]. National bioethanol production data were obtained from ePURE for 2023, which reports installed bioethanol production capacity for each European country [144]. This data source is consistent with the methodology applied by Rodin et al. [14], who similarly relied on ePURE key figures to estimate fermentation-related CO₂ emissions. The total installed production capacity for bioethanol for the EU's 27 member states is estimated at 8.23 billion liters, whereas the biogenic CO₂ emissions of bioethanol plants was 6.13 Mt in 2023 consistent with previously reported estimates of 4.4–5.7 Mt [14,25,144,146]. The calculated emissions represent process-related biogenic CO₂ released during fermentation and exclude emissions related to upstream biomass supply and downstream fuel use.

Other by-products include alcohols (ethanol, propanol, butanol, amyl alcohol, glycerol, phenethyl alcohol), acids (acetic, caproic, caprylic, lactic, pyruvic, succinic), esters (ethyl acetate and any other combination of acids and alcohols), acetaldehyde, diacetyl, and H₂S [147]. Alcohol is generated by yeast as by-products from ethanol fermentation. Sulfite also can be produced via yeast metabolism due to the sulfate assimilation pathway, in which yeast consumes sulfate to produce sulfur-containing amino acids that can also produce sulfite [148]. The produced sulfite depends on the yeast species, fermentation conditions, and sulfur-containing compounds in the feedstock [149].

The fermentation process generates a considerable amount of CO₂ as by-product. Concurrent to the stoichiometric equation, the gas produced during the fermentation consists of up to 99–100% CO₂ [25], with CO₂ being the main by-product of ethanol fermentation: $C_6H_{12}O_6 \rightarrow 2 C_2H_5OH + 2 CO_2$. CO₂ derived from bioethanol production possesses a level of purity suitable for direct utilization in industries such as food and beverage or pharmaceuticals [26], where the quality standards for CO₂ used in these industries are exceptionally stringent and dictated by organizations like the European Industrial Gases Association and the International Society of Beverage Technologists [14,150]. However, while the regulations are strict, certain impurities such as water, oxygen, hydrocarbons, and carbon monoxide (CO) may be also apparent in those gases [14]. Due to the potential purities and advantages of this sector, methanol production using renewable hydrogen and biogenic CO₂, derived from bioethanol plants, has been investigated in many past works [25,151–153].

4.5. Food and Beverage Industry

The food industry contributes significantly to GHG emissions through four main sections: livestock and fisheries (31%), crop production (27%), land use (24%), and supply chains (18%). Food processing, which involves energy and resource consumption, contributes around 1% of global emissions. While transportation only accounts for 6% of a food item's emissions, tackling supply chain inefficiencies and food waste is crucial, as a quarter of food production emissions are lost as waste [154]. Measures like durable packaging, refrigeration, and efficient processing can help mitigate waste and reduce emissions, but addressing emissions from food production remains a significant challenge. Efforts to minimize waste, improve efficiency, and develop low-carbon food technologies are essential to sustainably meet rising food demands. Due to the diversity of the involved section in the food industry and the distribution of the CO₂ emissions across the complete value chain, it is a challenge to capture and use the emitted bio-CO₂ in this section of the food industry.

Fermentation is a process carried out by specific microorganisms to modify the texture of foods, preserve them through the production of acids or alcohol, or improve their flavors and aromas. It is essential in creating a variety of food and beverage products, including

beer and wine (alcoholic fermentation), as well as dairy products, vegetables, meat, and fish (lactic acid fermentation). As also stated in Section 4.4, fermentation is the main process applied for bioethanol production. In alcoholic fermentation, yeast converts simple sugars into alcohol, usually in an anaerobic environment with temperatures between 8 and 30 °C, and carbon dioxide is a by-product of this process [24]. Lactic acid fermentation, on the other hand, converts sugars like lactose into lactic acid and other minor components, reducing pH levels, which is essential for taste, aroma, and product preservation. This process is also anaerobic and typically occurs at temperatures between 20 and 40 °C [15,155].

Wine making involves harvesting grapes, crushing them to release sugars and juice, fermenting the juice with yeast to produce ethanol and carbon dioxide, clarifying the wine, aging it for further development, and finally bottling it for consumption. For certain wines, carbonation is also necessary. Beer production begins with mashing malted barley grains to create fermentable sugars. The resulting liquid, called wort, is boiled with hops for the bitterness, flavor, and aroma. After cooling, yeast is added to ferment the sugars into alcohol and for carbonation, which then undergoes conditioning to develop its flavors before filtering, carbonating, and packaging for distribution.

On-farm production is typical for EU wines, and in 2020, there were 2.2 million vineyard holdings in the EU, varying greatly in size. Romania is the EU country with the most vineyard holdings, whose 800,000 holdings made up 37.9% of all vineyard holdings in the EU. Vineyards have various average sizes in different EU countries: an average size of 0.2 hectares in Romania to over 10 hectares in France, accounting for 3.2% of holdings in the EU, but corresponding to 59.2% of the land used in wineries [156]. According to the International Organization of Vine and Wine, Europe is the largest producer in the world, with 61% of global wine production taking place in Europe, with 15,000 million liters of wine being produced in 2023. Italy was the world's largest wine producer, followed by France and Spain accounting for 47% of global production [156,157].

In the same manner as in the bio-ethanol industry, bio-CO₂ in the FAB industry is mainly produced during the fermentation process, where sugars are converted into alcohols. The fermentation process is the main process applied in the production of beer and wine and results in high-purity biogenic CO₂. The CO₂ from fermentation processes in the FAB industry, such as beer brewing and wine production, lead to considerable amounts of CO₂ [26]. The volume of bio-CO₂ emissions from the FAB industry in each country was estimated based on annual beer and wine production in the EU. For beer, it was assumed that 37 g of bio-CO₂ per liter is emitted during production (assuming 5% alcohol vol.) [14,158,159], and for wine with an average alcohol content of 12 vol. %, approximately 88 g of CO₂ per liter is released during production [14,157]. Based on this, the calculated bio-CO₂ emission from beer and wine production were 1.22 and 1.67 Mt, respectively, amounting to 2.88 Mt in 2023 for the FAB sector, which is in the range 2.5–2.92 Mt reported in similar studies [14,160].

For the case of the wine industry, it is particularly affected by seasonality. In particular, the wine industries present a relatively pure bio-CO₂ stream, with lower contribution to the total EU bio-CO₂ streams [6]. However, the emissions are directly related to the grape harvest season that in most regions is conducted in late summer, and the annual CO₂ production is concentrated in approximately three months [161]. On the other hand, beer production is also to some extent influenced by seasonality since some beers are brewed all year round and others are seasonally brewed or once a year. Beer production units are widely distributed among breweries and microbreweries; demand could also affect the brewing process and consequently the bio-CO₂ emissions [162]. Since high-quality bio-CO₂ is produced, in many cases it can be reused within the same industry for the carbonation of beverages or for packaging. In combination also with the low emissions per plant and

their wide dispersion, it presents several challenges regarding their scalability for bio-CO₂ utilization. During the fermentation process, breweries and wineries often release carbon dioxide at a significantly higher rate than what is required for carbonating beer or wine and pressurizing lines within the facility. Despite this, it is common practice for these establishments to vent all the carbon dioxide produced during fermentation and procure carbon dioxide from external suppliers, instead of storing, conditioning, and reusing the internally produced CO₂ [14,15].

4.6. Direct Air Capture Plants

While most plants can only capture between 50 and 90% of their emissions, the remaining CO₂ eventually enters the atmosphere. Even in an optimal industrial setup where CO₂ is fully captured onsite, it still remains challenging to directly apply end-of-pipe capture systems to CO₂ emitted by the transport sector and in particular the maritime sector [163]. Although Direct Air Capture (DAC) plants are not directly related to upstream biomass-related processes, they can provide solutions in this context.

DAC is an innovative technology designed to address climate change by extracting CO₂ directly from the atmosphere. Its versatility in reducing CO₂ emissions regardless of the emission source location makes it a promising technology in combating climate change [164]. In other words, it can be implemented theoretically anywhere without geographical restrictions and in proximity with CO₂ utilization sites [165]. DAC systems employ various sorbents, typically basic in nature due to the acidity of the CO₂ gas, such as alkaline carbonates and amine solutions, to efficiently capture CO₂ from the air [166]. CO₂ is initially absorbed and then released from the sorbent, returning it to its original state for subsequent capture cycles [163]. After the CO₂ is captured from the air, it can then be either stored underground or further utilized for the production of added value chemicals and fuels such as methanol [167,168].

DAC technologies can achieve CO₂ purities exceeding 95%, with redox and cryogenic approaches offering purity levels up to 100%. Purity levels for hydroxide-carbonate and Temperature Vacuum Swing Adsorption (TVSA) approaches depend on the operating conditions and sorbent type, while membrane-based approaches require multiple separation levels to attain practical purity ranges [169]. However, current energy consumption rates and the costs of DAC exceed those of point-source capture technologies. This is primarily due to the dilute nature of atmospheric CO₂ compared to the concentrated CO₂ in industrial emissions, leading to higher energy requirements and costs for DAC relative to other technologies [170]. Current large-scale DAC implementation is also limited, with only around 10 kt CO₂ captured globally by 27 commissioned plants in Europe, North America, Japan, and the Middle East. In the International Energy Agency (IEA) Net Zero Emissions by 2050 Scenario, DAC technologies are projected to capture over 85 Mt of CO₂ in 2030 and nearly 980 Mt CO₂ in 2050, necessitating a significant scale-up from the current capture levels [170].

5. Assessment of EU Maritime Methanol Production from Bio-CO₂

Building on the findings of Section 4, Section 5 critically assesses the technical feasibility and infrastructure readiness for scaling up e-MeOH production in the EU, addressing the challenges related to sourcing renewable feedstocks and the supporting supply chain. First, the current and projected availability of bio-CO₂ is compared with the required volumes for methanol production. Next, the geographic distribution of these emissions is examined in order to identify which regions hold the highest potential, as well as the associated logistical challenges of establishing an EU-wide supply network. Green hydrogen production capacity and targets, for EU as a whole and at national levels, are then assessed

in relation to the projected demand. The analysis concludes with a review on the readiness of methanol storage and bunkering infrastructure at European ports in comparison also with the findings from the previous sections.

5.1. Bio-CO₂ Distribution and Availability

Based on the findings of Sections 4.1–4.5, it was estimated that approximately 350 Mt of biogenic CO₂ were emitted in 2023 from EU's 27 member states. The majority of these emissions originated from the production of heat and power (64.3%), followed by pulp and paper production (21.2%), biogas and biomethane (11.9%), bioethanol (1.8%), and the FAB industry (0.8%). The complete methodological process in estimating the EU bio-CO₂ emissions is provided in a consolidated form in Table A1 in the Appendix A section. While uncertainties remain, due to the heterogeneity of bio-CO₂ emitting sectors and inconsistencies in emissions reporting across countries and facilities, this estimate falls within the range reported in similar studies (154–506.7 Mtpa) [6,14]. Building on these results, it is important to compare these quantities and their availability with the fuel demand of the EU maritime sector, as well as the estimated future bio-CCU volumes (projected by the EU JRC) [171].

Figure 7 illustrates the bio-CO₂ requirements to produce e-MeOH at a scale sufficient to replace a portion of the sector's energy needs alongside projected bio-CO₂ capture and utilization volumes [171,172]. The estimated values were based on the assumption that 70% of the total CO₂ feed is converted to methanol assuming optimized industrial reactor conditions and configurations [43]. The maritime industry needs were based on data involving the total CO₂ emissions of the EU maritime sector, the average GHG intensity of the maritime sector, and assuming an average marine engine efficiency of 35% [173,174]. The results show that replacing 0.5% of the EU maritime needs with e-MeOH would require approximately 2.7 Mtpa of bio-CO₂, whereas a 5% replacement would require 26.8 Mtpa. In both cases, the required bio-CO₂ quantities amount to almost the complete amount projected for bio-CCU in 2030 [171], corresponding to 0.77% and 7.7% of the total theoretical available amount of bio-CO₂. On the other hand, for a 10% replacement, the demand would reach 53.6 Mtpa, significantly exceeding the projected bio-CCU volumes for 2050 and requiring approximately 15.4% of the theoretical available bio-CO₂. In all cases, bio-CO₂ will also be utilized towards the production of other e-fuels such as Sustainable Aviation Fuels (SAFs) and products [6], and therefore, the share available for e-MeOH synthesis will eventually be significantly lower than the projected amounts.

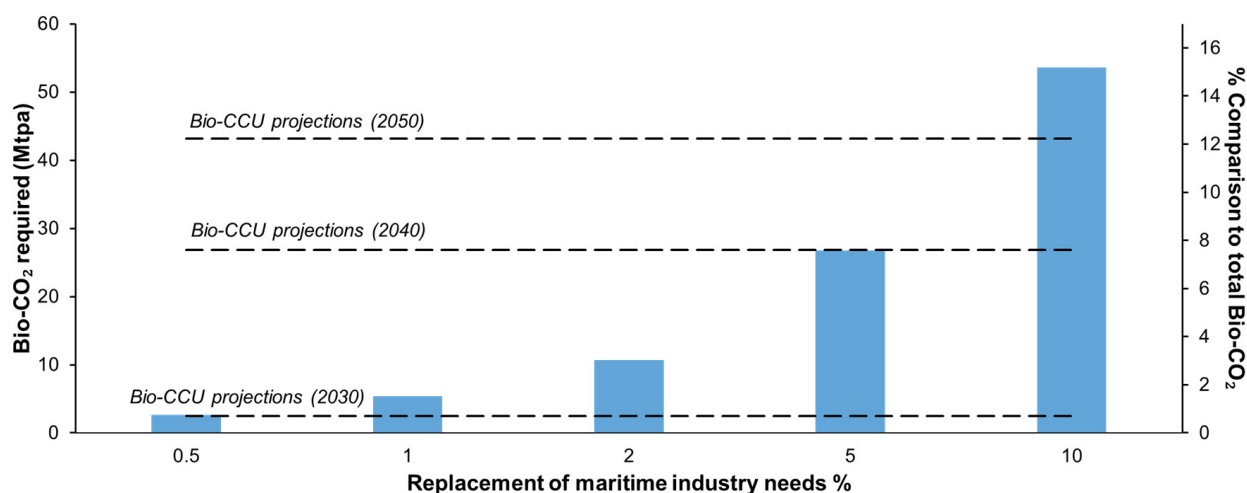


Figure 7. Bio-CO₂ requirements as a function of maritime industry needs percentage.

Apart from evaluating the EU bio-CO₂ as a whole, it is also important to locate those emissions across Europe, as well as the sectors from which they originate. In Figure 8, the distribution of bio-CO₂ emissions across the EU is illustrated alongside the contribution of each emitting sector to each country's total emissions [14,89,105,113,114,132,144,146,157,159,160,175,176]. The results show that the availability of bio-CO₂ is not concentrated in only a few countries but is instead decentralized with certain regions exhibiting higher emissions than others. For instance, Nordic countries account for over half of the total emissions, with Sweden and Finland representing 17.3% and 15.3% of the total emissions, respectively. This is mainly due to their extensive forest resources, along with waste and peat, which serve as a feedstock for heat and power generation [177,178]. Additionally, Sweden and Finland are considered to be among the world's largest pulp and paper producers, accounting for 60% and 18% of the EU total pulp and paper production in 2023 [179]. Germany also presents significant potential in e-MeOH production, accounting for 13.8% of the total bio-CO₂ emissions due to the country's highly developed bioenergy sector [105]. A significant share of Germany's total energy supply comes from biomass in the form of heat and power plants, whereas it also leads the biogas sector with nearly 10,000 plants in operation [180]. Other countries with significant shares in bioenergy and therefore bio-CO₂ emissions include Italy, France, Poland, Spain, the Netherlands, Denmark, and Austria [105]. The above EU countries report high volumes of renewable CO₂ emissions; however, these are primarily associated with the bioenergy and the pulp and paper sectors. As mentioned in Sections 4.2 and 4.3, these sources generate significant bio-CO₂ emission, but the resulting streams are typically diluted, making capture more costly. On the other hand, smaller but higher-purity CO₂ streams are produced in the biogas sectors led by Germany and Italy and the bioethanol/FAB industry in countries such as Germany, France, and Spain.

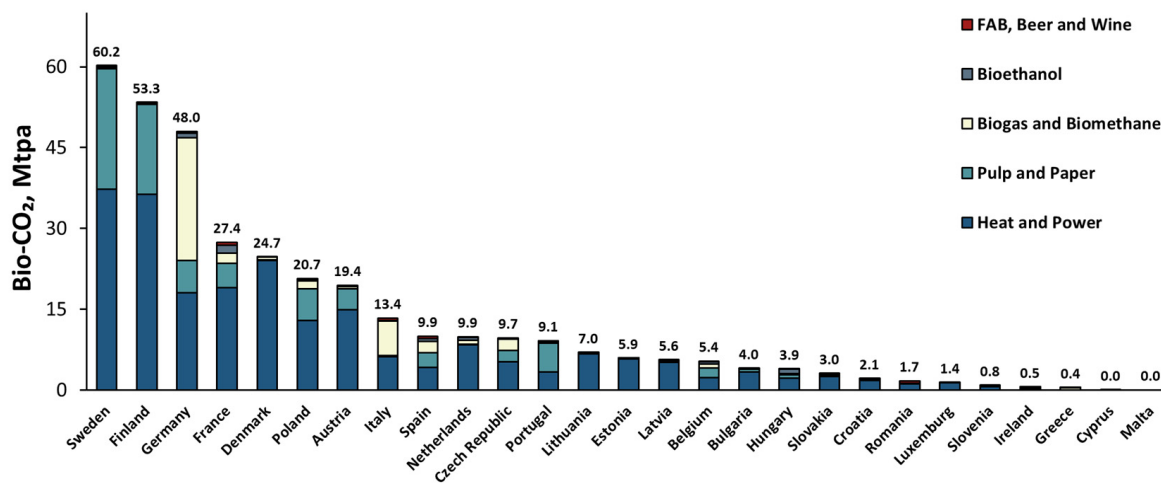


Figure 8. EU bio-CO₂ emissions by country and sector (2023).

The decentralized nature of bio-CO₂ emissions in the EU indicates that e-MeOH production in regions with limited biogenic emissions, but with a developed maritime sector (and thus increased fuel demand), will require the construction of an EU-wide CO₂ transportation network. A system of this scale would facilitate cross-border CO₂ transport, connecting high-emission regions with optimal production and demand centers [181,182]. This potential network would help overcome regional feedstock limitations and reduce overall costs for production, but its construction entails significant technical, economic, and legal challenges [181,183]. Initially, these transport systems are expected to be established at a regional or national level, designed to accommodate multiple bio-CO₂ sources and

industries [184], which introduces complexities in handling CO₂ streams with varying purities, compositions, and flowrates. These differences will require sector-specific conditioning and capture techniques, complicating efforts to standardize the capture process and thus streamline logistics and reduce costs. A CO₂ hub-clustering approach could be utilized where smaller bio-CO₂ emitters would be aggregated through a shared pipeline system to a centralized hub and temporary storage would allow for the accumulation of sufficient CO₂ volumes to enable continuous and economically viable methanol production [185]. Direct air capture plants could also provide solutions to the logistics of CO₂, if larger deployments and cost reductions are achieved. Regarding transportation, given the large volumes of CO₂ involved, high-pressure pipelines are expected to be the primary transport method, though ship-based transport will also play a role, particularly for linking ports and CCU/S hubs [184]. Key ports such as Rotterdam are already investing in CO₂ storage, conditioning, and bunkering facilities [11], whereas liquefied CO₂ carriers are currently in order by ship companies [186]. Apart from technical and economic considerations, the development of an extensive CO₂ transport infrastructure (whether onshore or offshore) entails significant legal and regulatory challenges, requiring multiple permits often with conflicting regulatory requirements [181,183].

5.2. Green Hydrogen Distribution and Availability

In this section, the hydrogen requirements for methanol synthesis are evaluated and compared to the current and planned green hydrogen production capacities across the EU. As illustrated in Figure 9 (assuming an electrolyzer efficiency of 50 kWh/kg H₂, 80% capacity factor, and stoichiometric hydrogen requirements for MeOH synthesis) replacing 0.5% of the maritime needs would require approximately 0.4 Mtpa of green hydrogen, corresponding to approximately 2.8 GW of installed electrolyzer capacity. Until September 2024, only 385 MW (0.065 Mtpa) were operational, making near-term production at this scale unlikely [187]. Scaling up to a 10% replacement would require around 8 Mtpa of green hydrogen and nearly 58 GW of electrolyzer capacity. By 2030, EU targets the domestic production of 10 Mtpa of renewable hydrogen and another 10 Mtpa imported from third countries, suggesting that such volumes could potentially become available in the future. However, based on the current installed capacity and expected progress, Hydrogen Europe estimates that only 1.7–3 Mtpa of renewable hydrogen will actually be available by 2030 [187,188]. Additionally, a large share of the green hydrogen supply is expected to be allocated towards other sectors such as ammonia synthesis, refineries, and the steel industry [187]. Despite these constraints, the EU plans to scale up green hydrogen production to 65 Mtpa in the long term [189], which could also support a large share of the maritime sector decarbonization.

Apart from the hydrogen targets for the EU as a whole, it is important to assess the distribution and capacity of operational and under-construction green hydrogen production facilities across Europe. As it stands, Germany is the main contributor to green hydrogen production, accounting for 13.6 ktpa or 29% of the total capacity with goals of expanding it by adding another 150 ktpa by 2026 [190]. Spain and Sweden follow, accounting for 6.5 ktpa (14%) and 5.4 ktpa (12%), respectively [190,191]. The presence of numerous water electrolysis projects under the clustering point in Northern and Western Europe suggests a focus on integrating green hydrogen into industrial and energy sectors, leveraging their abundant wind power sources. Countries in south Europe (e.g., Spain) benefit from increased solar and could become major contributors to green hydrogen production. In the future, Sweden plans to increase its current production to 150 ktpa, while France targets 40.5 ktpa by 2026 [190]. Additionally, Germany, France, and Denmark show the highest

ambitions for 2030, and the Netherlands recently revised its 2030 goal from 4 GW to 8 GW by 2032 [187].

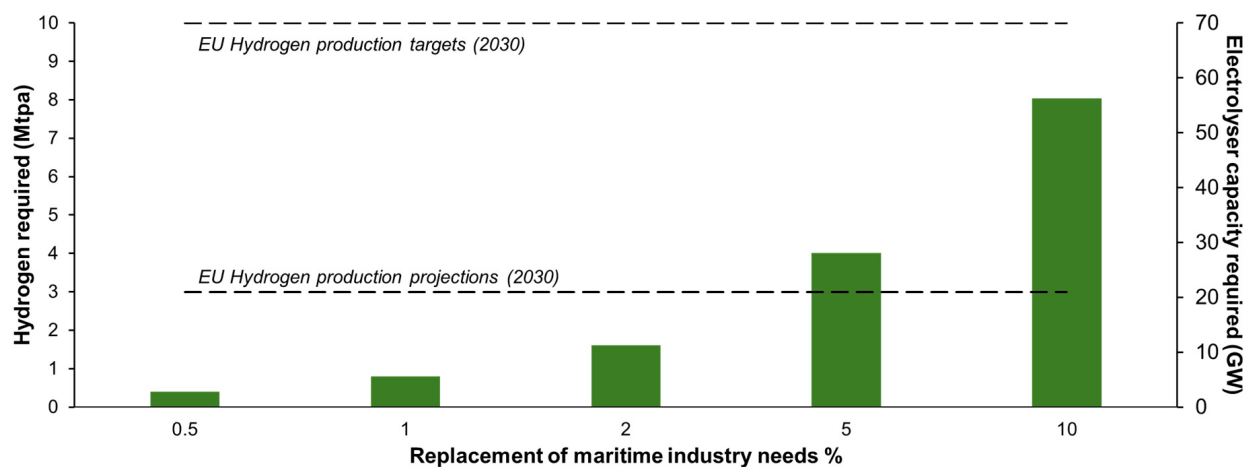


Figure 9. Green hydrogen requirements as a function of maritime industry needs percentage.

Overall, assuming an electrolyzer efficiency of 50 kWh/kg H₂, the electricity-only cost component for hydrogen production scales linearly with the electricity price (e.g., 30–70 €/MWh corresponds to ~1.5–3.5 €/kg H₂ for the electricity input alone), which is also a critical factor for the establishment of this process. Total hydrogen costs depend additionally on capital costs, utilization factors, logistics, and financing schemes [192]. A potential solution in sourcing renewable hydrogen for e-MeOH production is the development of EU-wide clustering activities such as hydrogen valleys. These clusters aim to geographically co-locate hydrogen production, storage, and end-use, minimizing long-distance transportation and enabling capital investment reductions [13,193]. Hydrogen valleys could be also located near sites with vast renewable energy capacities, minimizing the production cost of H₂ and focusing on connecting the hydrogen supply to consumption locations, even at an international scale. They are emerging throughout Europe and can involve their co-location with major bio-CO₂ industrial emitters such as pulp and paper or bioenergy production facilities [13,193,194]. This geographic proximity simplifies the logistics of capturing CO₂ and synthesizing methanol onsite or nearby, reducing transportation costs. Hydrogen valleys can also be used for multiple end uses, such as mobility, industrial processes, power, and synthetic fuels, and thus stabilize the demand for renewable hydrogen [195]. This could render investments in large-scale electrolyser capacity more viable, supporting simultaneously the green hydrogen needs of e-MeOH production.

5.3. Maritime Fuel Demand and Methanol Production Capacities

Following the assessment of the technical and logistical challenges in sourcing bio-CO₂ and renewable hydrogen, this section examines the expected short- and long-term demand for e-MeOH, as well as the requirement to replace a certain share of the maritime sector. Furthermore, an outline of the methanol storage and bunkering infrastructure is provided, which will influence the pace and scale of adoption.

Policy developments in recent years have sought to accelerate the uptake of renewable fuels such as e-MeOH in the maritime sector. For instance, in January 2024, the European Union has extended the EU ETS system to include CO₂ emissions from all large ships (>5000 GT) [196]. Additionally, the FuelEU Maritime Regulation was established in an effort to promote the use of renewable, low-carbon fuels for shipping [197], whereas the IMO revised its current GHG strategy, incorporating measures to develop infrastructure that supports the supply of zero or near-zero GHG emission fuels [1].

Another factor that could shape the future of large-scale e-MeOH production is the available infrastructure for MeOH storage and distribution. Methanol already has an established market in the chemical industry and is actively traded and transported worldwide, meaning that the storage infrastructure along with the required safety protocols are in certain cases already established. Currently, 120 ports are equipped with methanol storage facilities, and many are setting new methanol bunkering rules [11]. Major European ports, including Rotterdam, Hamburg, and key locations in Scandinavia, are actively expanding their bunkering capabilities to support methanol. As methanol remains a liquid at ambient conditions, its bunkering process is similar to that of conventional maritime fuels, requiring only minor and cost-effective modifications to the existing infrastructure [11].

Figure 10 shows an overview of (a) the potential bio-CO₂ emissions, (b) green hydrogen production capacities, and (c) methanol infrastructures at European ports and (d) promising EU regions that possess large quantities of bio-CO₂, green hydrogen production capacities, and future expansion plans, as well as port bunkering and storage infrastructures. These developments align with the findings from Sections 5.1 and 5.2, suggesting a correlation between ports investing in methanol infrastructure and regions with high concentrations of renewable feedstocks. Indicatively, countries such as Germany, Sweden, the Netherlands, Belgium, Denmark and France which, concentrate approximately 50% of the total bio-CO₂ emissions, promoting ambitious green H₂ targets, are also among the most active in the development of methanol storage/bunkering infrastructures.

This alignment in renewable feedstock availability and infrastructure readiness is most pronounced in the Antwerp–Rotterdam–Amsterdam (ARA) region, which might serve as the primary implementation area of maritime e-MeOH. Two of the most active EU bunkering ports are located in the ARA region, namely the Port of Rotterdam and Antwerp-Bruges, which exhibit the ongoing and planned development of large-scale CO₂ transport and storage networks along with the parallel scaling of the green hydrogen supply, creating favorable conditions for maritime methanol value chains.

In the Port of Rotterdam, the Aramis project is expected to establish a 22 Mtpa CO₂ collection hub and offshore transport and storage infrastructure by 2030, connecting the port to depleted gas fields in the North Sea [198]. This system is planned to expand through the Delta Rhine Corridor, enabling CO₂ and hydrogen transport towards the Ruhr area and establish cross-border links among Antwerp, Zeeland, and Rotterdam [199]. The port of Antwerp-Bruges is also developing CO₂ collection and liquefaction infrastructure to enable offshore transport and storage [200]. Although these projects are primarily designed for CO₂ storage, they demonstrate the active development of shared infrastructure. Facilities such as collection hubs, liquefaction plants, storage terminals, and cross-border pipelines could later be repurposed to connect bio-based facilities with production plants, where bio-CO₂ would serve as a feedstock for maritime e-methanol.

Regarding green-H₂, the ARA region is also advancing large-scale electrolysis deployment. While long-term targets exceed several gigawatts [201], near-term projections indicate more limited capacity, which may initially constrain hydrogen availability [202]. Nevertheless, combined domestic production plans and long-term hydrogen import strategies position the ARA region as a leading European hub for renewable hydrogen and thus for RFNBO methanol production [203].

To this end, Central/North European countries are expected to play an important role in this sector, whereas issues such as bio-CO₂ and hydrogen logistics (both domestic and cross-country) will define the technical and economic feasibility for the establishment of this technology.

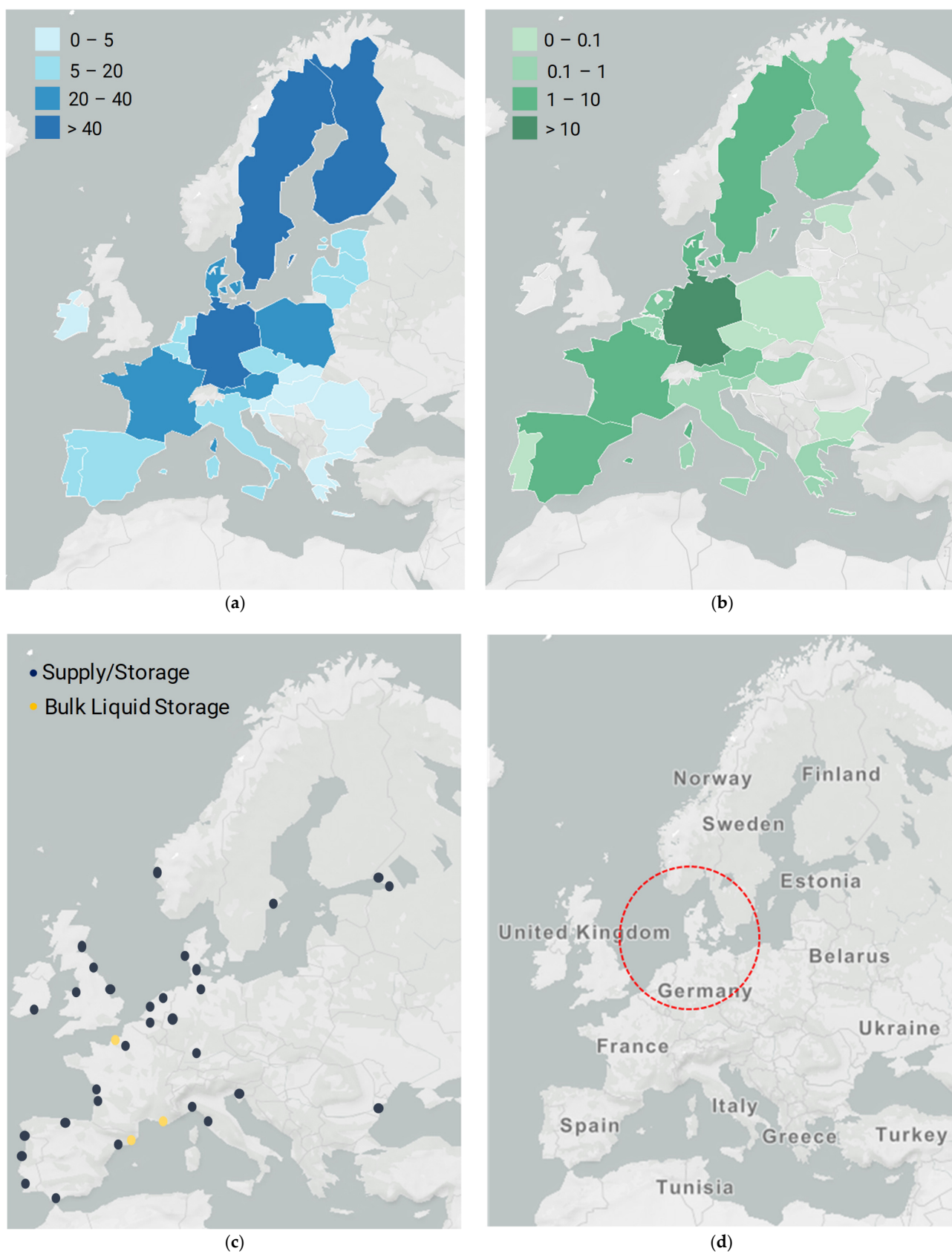


Figure 10. (a) Bio-CO₂ emissions (Mtpa) in 2023 (data from [14,89,113,114,132,144,146,157,159,160,175,176]); (b) Green hydrogen production capacity (ktpa) in 2023 (data from [204]); (c) Current status of port methanol storage and bunkering infrastructure in the EU in 2022 (data from [205]); (d) Promising EU regions possessing availability in bio-CO₂, green hydrogen and port infrastructures.

6. Research Needs and Future Direction

The analysis conducted in the previous sections showed that transitioning towards a sustainable maritime methanol value chain based on biogenic CO₂ is technically feasible but requires targeted research to overcome current technical, economic, and infrastructural bottlenecks. More specifically, gaps are identified relating to data quality, stream characterization, infrastructure design analysis, and system-level assessments.

The heterogeneity of bio-CO₂-emitting processes creates significant gaps in consistent identification and reporting across sectors. Future research should prioritize the development of harmonized monitoring and reporting frameworks at the EU and international level. Particular attention is required for biomass combustion and pulp and paper facilities, where mixed biomass feedstocks and in some cases co-firing with fossil fuels complicate the accurate attribution of biogenic CO₂ shares. In addition, the improved tracking of CO₂ streams is needed to distinguish between vented and already utilized streams. Establishing standardized methodologies and facility-level transparency will enhance data reliability and support more accurate resource mapping and infrastructure planning.

Accurate and extensive bio-CO₂ stream characterization and conditioning requirements are also lacking from the literature. Although data on the CO₂ composition and impurities exist, the detailed characterization of bio-CO₂ streams emitted from such facilities remains limited. To this end, systematic sampling and compositional analysis across facilities and sectors should be conducted, helping to identify critical impurities that may affect methanol synthesis catalysts and define appropriate cleaning and conditioning requirements. In parallel, the sector-specific optimization of CO₂ capture processes is needed to reduce energy demands and costs. Streamlining the capture, cleaning, and conditioning process is important to reduce costs and improve the economic competitiveness of maritime e-MeOH.

Infrastructure readiness and logistics have also emerged as significant bottlenecks in the wider establishment of this technology. Unlike fossil-based industries, bio-CO₂ emitters are smaller, more variable, and geographically dispersed. This limits the economic viability of standalone capture and utilization projects, as individual facilities often cannot reach economies-of-scale. Clustering approaches, where CO₂ from multiple emitters is aggregated before utilization, offer a practical pathway to scale. By aggregating larger volumes, clusters can justify shared investments in the capture, conditioning, storage, and transport infrastructure, while reducing project risk through standardized processing capacity. However, clustering introduces added logistical complexity, increased transport needs, and coordination challenges. Research that analyzes the spatial optimization of cluster configurations, balancing transport distances, the capture scale, and operational flexibility, will be essential for future development. Local constraints such as permitting, land availability, and existing infrastructure must also be incorporated into system-level planning.

All of the above considerations should be addressed through system-level analyses and on a case-by-case basis starting from port-level demand, for example in regions with the highest implementation potential, and trace all upstream requirements, seasonality aspects, and bottlenecks across the value chain. In addition, comprehensive techno-economic and environmental assessments are necessary to provide a realistic view of economic and environmental competitiveness with other renewable and conventional fuel options.

7. Conclusions

This study provides an initial assessment of the availability, quality, and distribution of biogenic CO₂ sources in Europe, with regard to their potential use for RFNBO methanol synthesis. Biogenic carbon dioxide emissions occur within the natural carbon cycle and arise as a by-product of biomass combustion, fermentation, and anaerobic digestion processes.

There are three main carbon capture approaches, pre-, post-, and oxy-combustion, and a wide range of commercially available separation techniques to isolate CO₂ from gas mixtures. Captured CO₂ can be handled and transported in gaseous, liquid, dense, or supercritical states. Potential impurities originating from the biomass feedstock may also be present in off-gases in various chemical forms. Common CO₂ impurities include nitrogen and sulfur-containing compounds, hydrogen cyanide, halides, siloxanes, heavy metals, oxygen, and water. Bio-CO₂-emitting sectors, including biogas, biomass power plants, pulp and paper mills, bioethanol production, and the food and beverage industry, exhibit significant variability in CO₂ emissions, purity, geographic distribution, seasonality, impurities profiles, and emission points.

The results of this work demonstrate that the deployment of RFNBO methanol in the European maritime sector is constrained not by the absolute availability of biogenic CO₂ alone, but by the combined interaction of CO₂ quality, geographic concentration, renewable hydrogen availability, and port infrastructure readiness. While total bio-CO₂ emissions in the EU amount to approximately 350 Mt in 2023, the system-level feasibility of utilizing this resource for marine use is strongly shaped by sectoral, spatial, and infrastructural mismatches.

A scenario-based analysis indicated that even modest levels of maritime fuel substitution impose significant material and energy requirements. Replacing 5% and 10% of fuel demands necessitates the use of large, diluted CO₂ sources from biomass combustion (214.6–298.2 Mtpa bio-CO₂) and pulp and paper industries (73.9 Mtpa bio-CO₂). Sources are generally characterized by low CO₂ concentrations (3–15% and 10–20%, respectively). More specifically, a 10% substitution level requires approximately 53.6 Mtpa of bio-CO₂, pushing the system toward sectors with higher capture complexity and costs. In addition, renewable hydrogen availability emerges as a critical bottleneck across all scenarios. For the same replacement, e-methanol would require electrolyzer capacities several orders higher than the current \approx 385 MW of the operational capacity in the EU, indicating a structural gap between targets and infrastructure deployment. At the country level, the analysis reveals a pronounced spatial mismatch among bio-CO₂ availability, renewable hydrogen, and maritime fuel demand. Several Member states exhibit substantial bio-CO₂ potentials but limited hydrogen production capacity, while others prioritize hydrogen development in regions that are weakly connected to major ports or a maritime bunkering infrastructure.

To bridge this gap, this research concludes that the future of e-methanol does not lie in isolated capture projects but in the development of integrated CO₂ hubs and hydrogen valleys. The aggregation of high-purity, decentralized sources (biogas/fermentation) with large-scale diluted streams (pulp/biomass) in strategic port locations such as Rotterdam and Antwerp, presents the possibility of achieving the necessary economies of scale. Future research includes the on-site sampling of actual bio-CO₂ streams, as well as the techno-economic analysis and optimization of the complete value chain.

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Abbreviations

The following abbreviations are used in this manuscript:

ARA	Antwerp-Rotterdam-Amsterdam
Bio-CO ₂	Biogenic Carbon Dioxide
CCU	Carbon Capture and Utilization
CHP	Combined Heat and Power
DAC	Direct Air Capture
EBA	European Biogas Association
EOR	Enhanced Oil Recovery
ETS	Emissions Trading System
EU	European Union
FAB	Food and Beverage
GHG	Greenhouse Gases
IMO	International Maritime Organization
JRC	Joint Research Centre
LFG	Landfill Gas
LNG	Liquefied Natural Gas
e-MeOH	Electrolytic Methanol
RFNBO	Renewable Fuels of non-Biological Origin

Appendix A

Table A1 presents the consolidated methodological framework used to estimate biogenic CO₂ emissions across the considered sectors in the EU-27 for 2023. It summarizes the data sources, calculation methods, key assumptions, emission factors, and uncertainty ranges applied in each case.

Table A1. Consolidated methodological framework for the estimation of sectoral biogenic CO₂ emissions in the EU-27 (2023).

Parameter	Biomass Combustion (Heat and Power)	Bioethanol	Biogas and Biomethane	Pulp and Paper	Food and Beverage
Data source	Eurostat; IPCC 2006 Guidelines	European Renewable Ethanol Association (ePURE)	European Biogas Association statistical report; Previous estimations from scientific publications	EEA industrial reporting (IED 2010/75/EU; E-PRTR Regulation (EC) No 166/2006)	International Organisation of Vine and Wine; The Brewers of Europe Association; Previous estimations from scientific publications
Bio-CO ₂ emission estimation	Bio-CO ₂ = CF × EF, where CF = biomass fuel input (TJ); EF = emission factor (kg CO ₂ /TJ)	Bio-CO ₂ = Ethanol volume (L) × 0.75 kg CO ₂ /L	Direct aggregation of estimated biogenic CO ₂ from literature	Direct aggregation of reported facility-level biogenic CO ₂	Beer: Volume (L) × 37 gCO ₂ /L; Wine: Volume (L) × 88 gCO ₂ /L

Table A1. Cont.

Parameter	Biomass Combustion (Heat and Power)	Bioethanol	Biogas and Biomethane	Pulp and Paper	Food and Beverage
Previous annual emissions estimations (Mt)	287–437	4.4–5.7 Mt	23 Mt (2017 study)	68 (2016 study), 92 (2020 study)	2.5–2.92
Annual Emissions estimation—this study (Mt)	214.6–298.2	6.13	41.3 (2023)	73.9 (2023)	2.88 (2023)
Reference	[14,15,25,26,105,113–115]	[14,25,89,144,146]	[25,89,90]	[132–134]	[14,157–160]

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