SEMPRE-BIO

D 4.1 Opportunities for the valorisation of CO_2 extracted from biogas (11/2023)

SEcuring doMestic PRoduction of cost-Effective BIOmethane

DBFZ

Beta
UVIC
UNIVERSITAT DE VIC
UNIVERSITAT CENTRAL DE CATALUNYA

Funded by the European Union

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PROJECT INFORMATION

GRANT AGREEMENT NUMBER	101084297
PROJECT TITLE	SEcuring doMestic PRoduction of cost-Effective BIOmethane
PROJECT ACRONYM	SEMPRE-BIO
FUNDING SCHEME	HORIZON-IA
START DATE OF THE PROJECT	1 November 2022
DURATION	42 months
CALL IDENTIFIER	HORIZON-CL5-2021-D3-03-16
PROJECT WEBSITE	https://sempre-bio.com/

DELIVERABLE INFORMATION

DELIVERABLE N°	4.1
DELIVERABLE TITLE	Report with the current state, progress made up to date and future challenges of advanced technologies for efficient CO_2 valorisation at multiple scales, from pilot to market scale, in the European Union
WP NO.	4
WP LEADER	UVIC
CONTRIBUTING PARTNERS	ACEA, BIOGAS-E, BIOREF, CET, CIC, DBFZ, DTU, Energigas, Envipark, Fraunhofer IEE, INV, RISE, UABio, UFZ, UVIC
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CONTRACTUAL DEADLINE	30.11.2023
DELIVERY DATE TO EC	30.11.2023
DISSEMINATION LEVEL	Public

DOCUMENT LOG

VERSION	DATE	AUTHORS	DESCRIPTION OF CHANGE
V1.1	12/07/2023	Velina Denysenko, Jaqueline Daniel-Gromke	Table of contents, initial version
V1.2	24/08/2023	Pablo Martin Binder, Laura Foix	Second version, additional chapter included
V1.3	02/11/2023	Velina Denysenko, Jaqueline Daniel-Gromke, Pablo Martin Binder, Laura Foix	Third version, further chapters completed
V1.4	15/11/2023, 16/11/2023	Lidia Paredes, Alejandra Córdova, Oriol Casal, Mario Ruiz	Internal review
V2.1	26/11/2023	Velina Denysenko, Jaqueline Daniel-Gromke, Pablo Martin Binder, Laura Foix	Compilation of feedback from reviewers, additional chapters included
V2.2	28/11/2023	Lidia Paredes, Alejandra Córdova, Oriol Casal, Mario Ruiz	2nd internal review
V2.3	30/11/2023	Velina Denysenko, Jaqueline Daniel-Gromke, Pablo Martin Binder, Laura Foix	Ready for submission

DISCLAMER

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Acronym Glossary

%-vol.: volume percent	**ISBT**: International Society of Beverage Technologists
£: British pound	**ISO**: International Organisation for Standardisation
€: euro	**JECFA**: Joint FAO/WHO Expert Committee on Food Additives
ºC: degree Celsius	**K**: potassium
a: year	**kg**: kilogram
A/S: stock-based corporation	**L**: litre
ACEA: ACEA Pinerolese Industriale SpA	**LCO_2**: liquid CO_2
AD: anaerobic digestion	**LLP**: Limited liability partnership
AG: joint-stock company	**LNG**: liquid natural gas
Al_2O_3: aluminium (III) oxide	**Ltd**: Limited
approx.: approximately	**m^3**: cubic meter
AS: stock-based corporation	**MAP**: modified atmosphere packaging
B.V.: limited liability company	**mill.**: million
BECCS: Bioenergy Carbon Capture and Storage	**MMA**: methyl methacrylate
bio-CNG: compressed biomethane	**mol**: mole
bio-LNG: biological liquefied natural gas	**MPa**: megapascal
BIOREF: Collaborative Laboratory for the Biorefineries	**Mt**: megatonne
C: carbon	**MTBE**: methyl tertiary-butyl ether
$CaCO_3$: calcium carbonate	**MW**: megawatt
CAGR: Compound Annual Growth Rate	**MWh**: megawatt hour
CAPEX: capital expenditure	**N**: nitrogen
CCS: Carbon Capture and Storage	**n**: number
CCU: Carbon Capture and Utilisation	**N_2**: molecular nitrogen
CH_3OH: methanol	**NH_3**: ammonia
CH_4: methane	**Ni**: nickel
CHF: Swiss franc	**NO**: nitrogen monoxide
CHP: combined heat and power	**No**: number
CIC: Consorzio Italiano Compostatori (The Italian Composting and Biogas Association)	**NOK**: Norwegian krone

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CNG: Compressed Natural Gas	**NO_x**: nitrogen oxides
CO: carbon monoxide	**NV**: public limited liability company
$CO(NH_2)_2$: urea	**O_2**: oxygen
CO_2 HCO_3^-: bicarbonate buffer system	**OPEX**: operational expenditure
CO_2: carbon dioxide	**P**: phosphorus
CO_3^{2-}: carbonate ion	**PBR**: photobioreactor
CuO: copper (II) oxide	**PBS**: polybutylene succinate
d: day	**PES**: polyethylene succinate
DAC(CS): Direct Air Carbon (Capture and Storage)	**pH**: potential of hydrogen (acidity)
DME: dimethyl ether	**PHA**: polyhydroxyalkanoates
DMFC: direct methanol fuel cell	**PHB**: polyhydroxybutyrates
e.g.: for example	**PPB**: purple phototrophic bacteria
e: electrical	**ppm**: parts per million
EC: European Commission	**PRPs**: requirements for prerequisite programmes
e-fuels: electrofuels	**PtG**: power-to-gas
EIGA: European Industrial Gases Association	**PtX**: power-to-X
Energigas: Energigas Sverige (Swedish Gas Association)	**PUFA**: polyunsaturated fatty acids
Envipark: Environment Park SpA	**resp.**: respectively
EOR: enhanced oil recovery	**RISE**: Research Institutes of Sweden
et al.: and others	**SAS**: joint-stock company
EU: European Union	**SCP**: single cell protein
EUR: euro	**SF**: state enterprise
FAO: Food and Agricultural Organisation of the United Nations	**SNG**: synthetic natural gas
Fraunhofer IEE: Fraunhofer Institute for Energy Economics and Energy System Technology	**SO_2**: sulphur dioxide
FSSC: Food Safety System Certification	**SpA**: joint-share company
g: gram	**STP**: standard temperature and pressure
GHG: greenhouse gas	**t**: tonne
GmbH: limited liability company	**th**: thermic
GWh: gigawatt hour	**TRL**: technology readiness level

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h: hour	**UABio**: Bioenergy Association of Ukraine
H_2: hydrogen	**UFZ**: Helmholtz Centre for Environmental Research – UFZ
$H_2NCOONH_4$: ammonium carbamate	**USD**: U.S. dollar
H_2O: water	**VFA**: volatile fatty acid
H_2S: hydrogen sulfide	**VOCs**: volatile organic compounds
ha: hectare	**vs.**: versus
HACCP: Hazard Analysis and Critical Control Point	**WHO**: World Health Organisation
HCO_3^-: bicarbonate	**wt%**: percentage by weight
i.e.: in other words	**ZnO**: zinc oxide
ibid.: in the same place	

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Consortium partners

Number	Project partner organisation name	Acronym
1	CETAQUA	CET
2	AIGUES DE BARCELONA	AB
3	CRYO INOX	CRYO
4	DEUTSCHES BIOMASSEFORSCHUNGSZENTRUM GEMEINNÜTZIGE	DBFZ
5	DANMARKS TEKNISKE UNIVERSITET	DTU
6	INVENIAM GROUP	INV
7	PROPULS	PROPULS
8	SINTEF AS	SINTEF
9	TERRAWATT	TERRA
10	TRANSPORTS METROPOLITANS DE BARCELONA	TMB
11	UNIVERSITEIT GENT	UGE
12	UNIVERSITAT DE VIC	UVIC
13	BIOGAS-E	BIOGAS-E
14	INNOLAB	INNOLAB
15	NATURGY	NAT
16	NV De Zwanebloem	MASS

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Executive summary

SEMPRE-BIO aims to demonstrate novel and cost-effective biomethane production solutions and pathways which maximise the carbon utilisation in the feedstock. Overall, the challenge is to decrease investment and operational costs, to optimise feedstock supply and use, to identify alternative and cheaper feedstocks, to improve plant efficiency and operations, to factor in the carbon savings and to increase and monetise co-benefits, from the commercialisation of side-products such as the digestate or the valorisation of residual gas streams.

Valorisation of biogenic CO_2 derived from biogas and biomethane plants in Europe represents a dynamic and steadily growing segment. In order to provide an overview on the options of biogenic CO_2 utilisation in different economic sectors in Europe in accordance with the deliverable D4.1, literature review and a survey were conducted with the latter being sent to all partners from SEMPRE-BIO as well as from three further European biomethane projects BIOMETHAVERSE (http://www.biomethaverse.eu/), HYFUELUP (https://hyfuelup.eu/), and METHAREN (https://metharen.eu/)[1]. These projects were encouraged by the European Climate, Infrastructure and Environment Executive Agency (CINEA) to contribute to common information and dissemination activities in order to increase the visibility and synergies between Horizon Europe supported actions and to address joint activities. Besides, external biomethane stakeholders from selected additional countries (the United Kingdom, the Netherlands, Germany and Poland) were contacted to participate in the survey due to the current and future relevance of biomethane production in combination with biogenic CO_2 valorisation in these countries.

The aim of the present report is to provide an overview of the current and future options of biogenic CO_2 valorisation derived from biogas and biomethane in Europe while mapping the biogas and biomethane sites capturing biogenic CO_2, the CO_2 production capacities as well as the valorisation sectors of captured biogenic CO_2. Thereby, the focus is on commercial-scale Carbon Capture and Utilisation (CCU) projects without further consideration of possible Carbon Capture and Storage (CCS) developments. This is due to the fact of the need of defossilisation of industrial sectors which can be achieved by replacing CO_2 of fossil origin by its biogenic counterpart against the background of the goal of the climate neutrality by 2050 in the European Union as stipulated by the European Climate Law.

Already today, the utilisation of the entire biomethane process chain including CO_2 valorisation for material and/or energy recovery results in ecological and cost benefits. Due to the expected rise of biogas and biomethane plant capacities in accordance with the target of 35 bcm of biogas and biomethane production in Europe by 2030, as defined within the RePowerEU plan as a part of the Biomethane Action Plan, more biogenic CO_2 from biogas and biomethane could be captured – more specifically, 46 Mt by 2030 and 124 Mt by 2050 according to European Biogas Association, 2022a. In combination with green hydrogen, biogenic CO_2 from biogas represents one possibility of CO_2 utilisation in order to increase amounts of synthetic biomethane.

There are different CO_2 valorisation routes ranging from the well-established to those still to be explored. The current report provides an overview of the selected options for valorisation of biogenic CO_2 from biogas such as in the agriculture, the food and beverage industry, the energy production and chemical industry based on their relevance for the SEMPRE-BIO project and the focus set on commercial CCU pathways. Within the scope of envisaged work in the SEMPRE-BIO project, special attention is given to the section 3.2 on production of value-added products such as biopolymers, biochemicals and alternative sources of protein from biogenic CO_2 along with insights into the production and cost framework. The report provides further an insight into the requirements for the use of the food-grade CO_2 uses, especially for, but also not limited to food and beverage industry. In addition, it delivers the mapping and listing of the biogas and biomethane plant sites with the CO_2 valorisation (current and

[1] The projects SEMPRE-BIO, BIOMETHAVERSE, HYFUELUP, and METHAREN are funded under the same call: HORIZON-CL5-2021-D3-03 (Sustainable, secure and competitive energy supply), topic: HORIZON-CL5-2021-D3-03-16.

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expected by the end of 2023) in Europe as well as the description of the selected project examples in European countries.

According to the literature review and survey conducted by DBFZ, Italy, the Netherlands, and the United Kingdom[2] are leading the way in biogenic CO_2 valorisation from commercial-scale biogas and biomethane facilities in Europe (60 % in total), followed by Germany and France (23 % in total).

With respect to the valorisation of biogenic CO_2 from the operating biogas and biomethane plants, the focus is currently on the air enrichment in greenhouses (35 %) and the use in the food and beverage industry (27 %). To a smaller extent, the captured CO_2 is used for Power-to-X technologies (10 %), for the production of dry ice or as a cooling agent (both at 8 %). Further utilisation sectors such as chemical industry, healthcare sector or pharmaceutics play a minor role. For the announced facilities, the CO_2 valorisation changes towards relative increase of CO_2 use in the food and beverage sector (47 %) as well as the increment of Power-to-X technologies (22 %). In contrast, the utilisation of CO_2 in greenhouses moves somewhat into the background (13 %).

Currently, biogas and biomethane sites are often far away from the industries with CO_2 demand, which might, however, change with the erection of new anaerobic digestion sites with CO_2 capture units or by merging the CO_2 produced at the different biogas and biomethane plant facilities via existing (as in the case of the Netherlands) or to be installed CO_2 pipelines. In combination with decentralised points of sustainable sources of, for instance, H_2 and N_2, small-scale and decentralised CO_2 production facilities from biogas and biomethane might enable creation of new sustainable business models.

The change towards the production of high-value biogenic CO_2-based products is not yet apparent, according to the announced and available targets. If biogenic CO_2 becomes scarcer, the competition for CO_2 worth transporting will increase. The competitive advantage of biogenic CO_2 from biogas and biomethane upgrading in comparison to its fossil-derived counterpart comprises proximity to customers, local and biogenic origin, green labelling, high purity grades, almost complete absence of impurities, safeguarded projected supply amounts, and possibility of the fixed non-seasonal price. The utilisation of CO_2 derived from biogas and biomethane with the greatest willingness to pay will then determine the price of this CO_2, while other types of valorisation may have to rely on the sub-segment of other sources. It can be expected that the highest prices for biogenic CO_2 will then be paid for the production of high-value CO_2-based products.

[2] Including Scotland and Northern Ireland.

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1. Introduction

As an introduction to the topic, the following depiction provides an overview of the objectives and the structure of the report, the possible sources of CO_2 and recovery of CO_2 from biomethane production.

In the course of the need of defossilisation of industrial sectors, the transition from fossil to biogenic CO_2 is necessary. Sources providing point-source CO_2, especially fossil, can be expected to decline over time, since increasingly more sectors of the economy will decarbonise (Comer et al., 2022). Biogenic sources of CO_2, such as those from biogas and biomethane plants, are therefore increasingly in demand. In its Communication on Sustainable Carbon Cycles the European Commission (EC) projects that by 2050 at the latest it will be necessary to capture carbon increasingly from biogenic sources with respect to the sustainable boundaries and without the negative impact on the environment or biodiversity (European Commission, 2021a).

In its AR6 Synthesis Report on Climate Change 2023, the Intergovernmental Panel on Climate Change classifies carbon sourced from biogenic sources along with – depending on its availability - Carbon Capture and Utilisation as an instrument in order to reduce emissions from the production and use of chemicals, while switching to low and zero greenhouse gas (GHG) emitting fuels such as ammonia, hydrogen or bio-based and other synthetic fuels is addressed as a decarbonisation pathway for light industry and manufacturing (IPCC, 2023). Within the anticipated by the 4th quarter of 2023 Industrial carbon management strategy after the public consultation round, the need to fully harness, along with others, the potential of Carbon Capture and Utilisation is addressed at the emerging market of carbon use to be created by 2030 while designing the milestones for 2040 and 2050, emphasising the limited supply and demand and required high capital investments (European Commission, 2023b).

According to the International Energy Agency, 2019, the global demand for CO_2 was calculated to be 230 Mt/a in 2015 and was projected to increase continuously in 2020 to 250 Mt/a and in 2025 to 272 Mt/a based on an average year-on-year growth rate of 1.7 %. Thereby, the specific numbers indicating CO_2 demand in Europe are not stated. The global CO_2 demand is driven first and foremost by the production of urea (57 %). Further, 34 % of the global CO_2 consumption can be attributed to the enhanced oil recovery (EOR), which is, however, primarily used in the United States and to a lower extent in Brazil, Canada, China and Turkey. The demand for the food and beverage sector as well as other applications plays a minor role at the global scale (both at 4,5 %) (IEA, 2019).

1.1. Objective and structure of the report

The objective of this report is to provide an overview of the current and future options of biogenic CO_2 valorisation derived from biogas and biomethane in Europe while mapping the biogas and biomethane sites capturing biogenic CO_2, the CO_2 production capacities as well as the valorisation sectors of captured biogenic CO_2. Thereby, the focus is on commercial-scale Carbon Capture and Utilisation (CCU) projects without further consideration of possible Carbon Capture and Storage (CCS) developments. This is due to the fact of the need of defossilisation of industrial sectors which can be achieved by replacing CO_2 of fossil origin by its biogenic counterpart against the background of the goal of the climate neutrality by 2050 in the European Union as stipulated by the European Climate Law.

To this end, the report is structured as follows:

- Section 1 provides the introduction with the brief comparison of biogenic and fossil sources of CO_2 and the description of recovery of biogenic CO_2 from biomethane production.
- Section 2 entails the description of the methodology of data collection differentiating between the literature review and conducting the survey carried out by DBFZ.
- Section 3 delivers an overview of different sectors for valorisation of biogenic CO_2, requirements for food-grade CO_2, the results of surveys and literature research with selected project examples of valorisation of CO_2 from biogas and biomethane in Europe, followed by the summary of future opportunities of biogenic CO_2 valorisation. Within the scope of envisaged work in the SEMPRE-BIO project, special attention is given to the section 3.2 on production of value-added products

such as biopolymers, biochemicals and alternative sources of protein from biogenic CO_2 along with insights into the production and cost framework.

- Section 4 contains the outlook.

1.2. Biogenic versus fossil sources of CO_2

The main fossil sources of CO_2 are represented by the cement production, steel and iron production, extraction of fossil fuels such as coal, natural gas and fuel oil, chemical production, and petrochemical products (Podder et al., 2023). In contrast to that, the main sources providing biogenic CO_2 are combustion of biomass, upgrading of biogas to biomethane, fermentation processes in the food and beverage industry (e.g., brewing or wine production) and bioethanol production with the latter also being based on fermentation but contrary to the food and beverage industry delivering the product which can be used as raw material or as a biofuel (Rodin et al., 2020). Further sources of biogenic CO_2 are represented by natural wells or phosphate rocks (EIGA, 2017).

An overview of biogenic and fossil sources of CO_2 with the typical CO_2 concentrations is provided in Figure 1. The biogenic sources of CO_2 are highlighted in dark green, whereas the fossil sources are left in light grey.

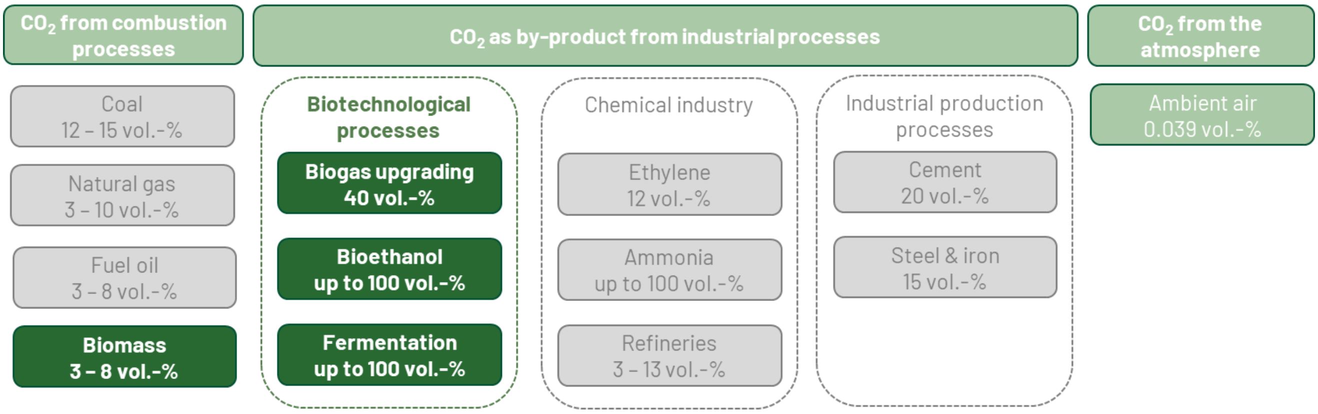

Figure 1: Overview of biogenic and fossil CO_2 sources with the available typical CO_2 concentrations (source: Rodin et al., 2020)

By minimising the CO_2 emissions from the point sources or by enhancing the use of CO_2, the reduction of CO_2 emissions can be realised (Adnan et al., 2019). With respect to the CO_2 emitting sources relevant are especially those with the high potential respectively (resp.) high CO_2 concentration which will with a high probability also be of interest in 2050 such as biogenic sources (Billig et al., 2019). The process of capture of CO_2 emissions in order to utilise the captured CO_2 flow is referred to as Carbon Capture and Utilisation (CCU). Thereby, CO_2 can be used either directly, which means without chemical or biological alteration, or indirectly, which stands for the transformation into the different products such as fuels, chemicals or building materials (IEA, 2019). In contrast to that stands the technology of Carbon Capture and Storage (CCS). The difference between CCU and CCS lies in the type of final use of captured CO_2. The CCS technology implies the capture of CO_2 from industrial flue gases and its transport, injection into the suitable geological site for the subsequent storage storage for a longer period of time, which is initially not defined (Chauvy and De Weireld, 2020; Cătuți et al., 2022).

In the public perception, the awareness of CCU within the nexus of climate change mitigation is still relatively low, whereas the acceptance of CCU-based products is relatively high with some exceptions for consumable goods from the food and beverage industry. Nevertheless, the overall acceptance for CCU technologies is higher in comparison to CCS. Based on empirical data collection, the support of political and industrial promotion, funding and investments into CO_2-derived products find consensus in the public. According to the survey conducted by Pieri et al., 2023, from the consumers' point of view, the willingness to pay for fuels based on recycled CO_2 is higher in comparison to food and beverages which corresponds to the purity requirements for CO_2 flow (Pieri et al., 2023). Consequently, the commercialisation and market uptake of CO_2-derived or CO_2-captured products with emphasis on

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product safety and environmental benefits is of high significance (ibid.). The safety of CO_2 derived from biogas plants for the application in the food and beverage industry in Europe was manifested in the document 70/17 Carbon Dioxide Food and Beverages Grade, Source Qualification, Quality Standards and Verification released by the European Industrial Gases Association in 2017 (EIGA, 2017). The quality standard requirements for biogenic CO_2 from biogas for valorisation in the food and beverage sector are described in detail in section 3.1.3 in Excursus 3.

The barriers to the development of CCS – beside the lower social and political acceptance in certain countries are of technical and economic nature defined by related development cost, economies of scale and technological innovation. Relevant for storage of CO_2 are also proximity and availability of storage sites (Ausfelder et al., 2022). The duration of the project realisation varies between CCU and CCS. Whereas biogenic CO_2 capture projects (CCU) take less than four years in the implementation, a few biogenic CO_2 Bioenergy Carbon Capture and Storage (BECCS) projects were implemented in approximately (approx.) seven years up to this point (International Energy Agency, 2023).

In its Communication on Sustainable Carbon Cycles the European Commission emphasises the need of carbon recycling from waste, sustainable biomass or from the atmosphere in order to replace fossil carbon and the promotion of technologies for CCU and production of sustainable synthetic fuels or other non-fossil-based carbon products by the sustainable bioeconomy and circular economy. In addition, EC addresses the need for the creation of an internal market for CCS in the form of Direct Air Carbon Capture and Storage (DACCS) and Bioenergy Carbon Capture and Storage (BECCS) (European Commission, 2021b). However, the DACCS technology represents currently a cost- and energy-intensive process due to the lower concentrations of CO_2 but is expected to gain more relevance in the future by sequestration of CO_2 from dispersed and diluted sources in the course of the envisaged technological maturity development (Rodin et al., 2020). In comparison to the CO_2 sourcing from ambient air, biogenic CO_2 from biogas and biomethane has comparative and cost advantage due to the higher CO_2 concentrations.

In order to achieve the goal of the climate neutrality in the European Union by 2050 as stipulated by the European Climate Law, it will be needed to capture between 300 Mt of CO_2 or more than 500 Mt of CO_2 from various sources depending on the chosen specific scenario to produce fuels and materials or for storage (European Commission, 2021a). Beside the CO_2 emissions reduction, the reasons for the use of CO_2 are technological competition, the expected availability of the surplus renewable energy delivering a cheaper source for CO_2 conversion leading to a more economical CO_2-based commodity materials, chemicals and fuels production, and energy security (IEA, 2019).

Today, about 2 Mt of biogenic CO_2 are captured per year, with 90 % being captured in bioethanol applications representing one of the lowest-cost technologies with the high CO_2 concentration in the process gas stream (International Energy Agency, 2023). However, when comparing the average CO_2 capture rates, biogas upgrading with 95 % is in the same range as CO_2 capture rate from bioethanol fermentation (Figure 2). What is more, CO_2 capture rate from biogas upgrading is in the same order of magnitude or even higher than that of most fossil-based pathways. Consequently, valorisation of biogenic CO_2 from biogas and biomethane production appears to be a logical and necessary step on the way to climate neutrality in Europe.

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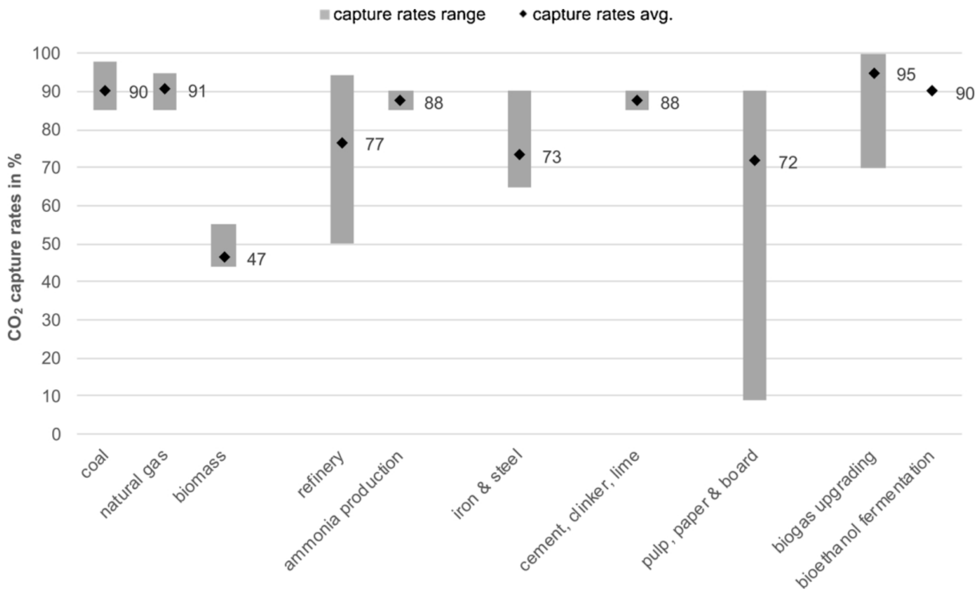

Figure 2: Available CO_2 capture rates from biogenic and fossil sources, ranges and average (source: Rodin et al., 2020)

Based on the biomethane production in 2020, Germany, Italy and the United Kingdom would be leading in biogenic CO_2 production in Europe. On the premise of 35 bcm of biogas and biomethane production in Europe (EU, EFTA countries[3], United Kingdom, Serbia and Ukraine), as defined within the RePowerEU plan as a part of the Biomethane Action Plan, and in case of all biogas being upgraded to biomethane by 2030, 46 Mt of biogenic CO_2 could be captured in parallel. If projecting 95 bcm of biogas and biomethane in Europe by 2050, 124 Mt of biogenic CO_2 were to be captured under the same assumptions (European Biogas Association, 2022a).

1.3. CO_2 recovery from biomethane production

Via anaerobic digestion (AD) of organic matter, biogas is produced containing 50–70 % of CH_4 and 30–50 % of CO_2, including minor components such as hydrogen sulphide (H_2S), nitrogen (N_2), oxygen (O_2), siloxanes, volatile organic compounds (VOCs), carbon monoxide (CO), and ammonia (NH_3). CO_2 and impurities have to be removed resulting in two steps of biogas treatment, namely cleaning (removal of minor unwanted components in biogas), and upgrading (removal of CO_2)(Adnan et al., 2019). The biogenic CO_2 captured in the course of biogas upgrading represents a climate-neutral and cost-efficient source of CO_2 which would be otherwise released into the atmosphere.

There are different technologies for biogas upgrading which with the exception of cryogenic separation divide the raw biogas into biomethane stream with > 90 % of CH_4 and secondary gas stream with 80-90 % of CO_2 (Kapoor et al., 2020). The by-product CO_2 gas stream can be captured but might contain trace compounds which have to be removed in order to employ the derived biogenic CO_2. The technologies for biogas upgrading depending on the CO_2 removal can be divided into absorption, adsorption, membrane, and cryogenic routes (Adnan et al., 2019).

In 2021, the membrane separation with 47 % was the most often used technology for biogas upgrading in Europe followed by water scrubbing with 17 %, chemical scrubbing with 12 %, and pressure swing adsorption with 10 %. The remaining 3 % were represented by physical scrubbing with 2 % and cryogenic separation with 1% (Figure 3).

[3] The European Free Trade Association (EFTA) countries comprise Iceland, Liechtenstein, Norway and Switzerland.

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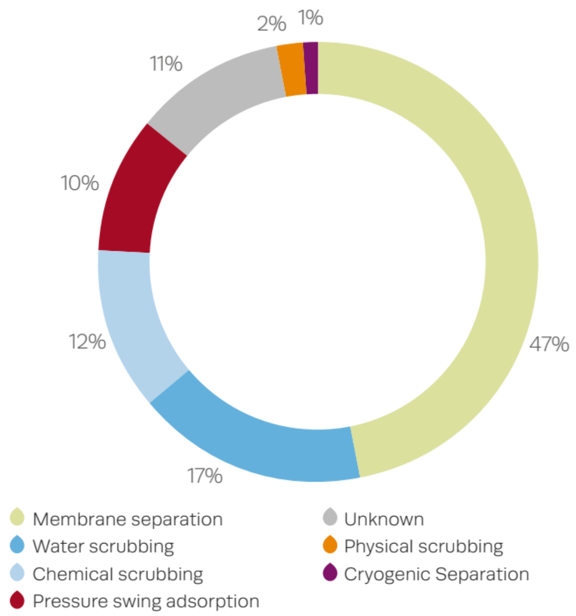

Figure 3: Biogas upgrading technologies in Europe in 2021, relative share (source: European Biogas Association, 2022b)

The choice of the specific biogas upgrading technology is decisive for the CO_2 concentration in off-gas: whereas amine scrubbing, pressure swing adsorption, and membrane separation feature up to 99%-vol. of CO_2, water scrubbing involving air stripping results in the lower CO_2 concentration in off-gas (Rodin et al., 2020). An overview of the trace compounds from the available commercial biogas upgrading technologies is presented in Figure 4.

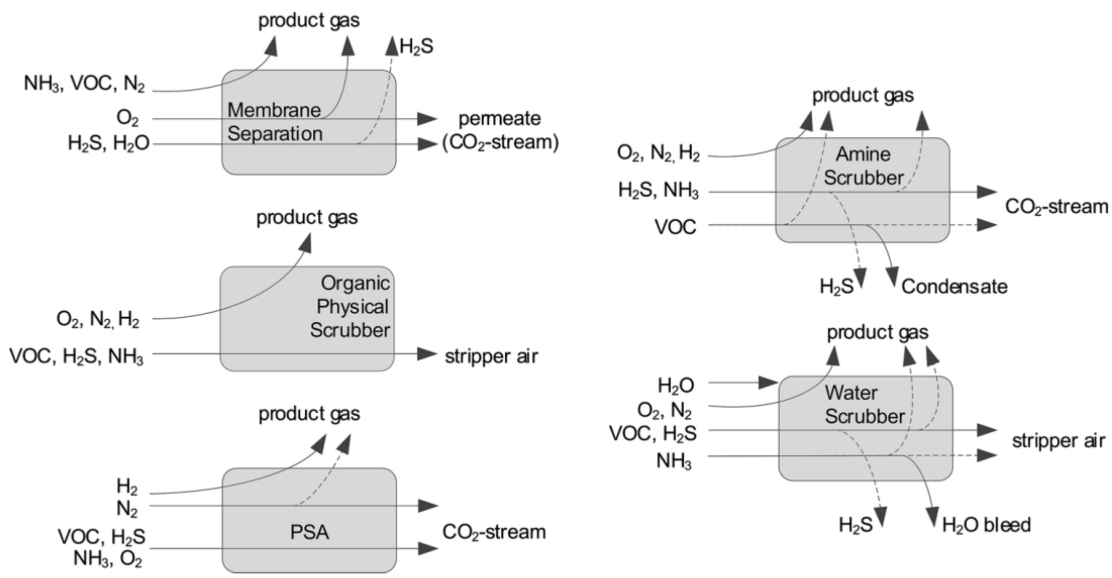

Figure 4: Trace compounds from the available biogas upgrading technologies (source: Rodin et al., 2020)

In addition to the recovery of biogenic CO_2 in the course of biogas upgrading, within the scope of SEMPRE-BIO project 5 innovative biomethane production technologies which will be demonstrated through 3 case studies based in Baix Llobregat (Spain), Bourges (France) and Adinkerke (Belgium) with CO_2 valorisation at different process stages will be investigated.

(1) Within the case study I at Baix Llobregat (Spain), the demonstration plant will be installed in the Baix Llobregat wastewater treatment plant (WWTP) which treats sludge through anaerobic digestion, currently producing 700 m^3/h of biogas. This biogas will be upgraded to biomethane

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by an innovative combination of two different technologies: proton exchange membrane water electrolysis (PEM) and CO_2 bio-methanation.

(2) In case study II in Bourges (France), the input gas for methanation is syngas instead of biogas, which is the most common approach (as in case study I). The demonstration plant consists of a combination of pyrolysis and bio-methanation to produce biogas from a novel feedstock, woody biomass, which is a non-digestible. This innovative combination of technologies is a patent of TERRA in which the woody waste goes through a thermo-chemical pyrolysis process producing pyrolysis gas, bio-oil and bio-char. Then the pyrolysis gas is cleaned and turned into syngas, which in turn is injected into a bio-methanation reactor to produce biogas. The biogas is upgraded to biomethane after a membrane separation system and directly injected into the gas grid.

(3) In case study III in Adinkerke (Belgium), the demonstration plant will be installed at the NV De Zwanebloem dairy farm which holds a permit for exploiting a biogas plant. The operator's goal is to co-digest manure and other agri-residues to optimise the process. The raw biogas produced in the anaerobic digestion will be upgraded through a cryogenic separation based on the phase separation due to the deep temperature decrease of the raw biogas mixture. The products of this cryogenic process are liquid biomethane, liquified carbon dioxide, water and hydrogen sulphide. Two different technological configurations will be designed and constructed to obtain value-added products from the liquified carbon dioxide and hydrogen: 1) hybrid fermenter and 2) solar photobioreactor.

In the SEMPRE-BIO project the cryogenic separation is used in case study III, as stated above. Cryogenic separation is the go-to technology when the target biomethane has to be liquified for transportation and additionally the liquid CO_2 (LCO_2) is of use (-150 ºC for the biomethane and -30 ºC for the CO_2), since it is also recovered. Using the same equipment for the liquefaction and also for the upgrading and polishing might be the key to reducing the CAPEX (capital expenditure) and the specific energy consumption linked to the carbon footprint for the whole process. However, a key point is the economic feasibility of low-capacity facilities (see Excursus 1). Finally, the overall evaluation (techno-economic assessment including GHG balances) of the innovative biomethane processes – carried out at the end of the SEMPRE-BIO project – will show whether and under what conditions the investigated processes can provide methane and CO_2 more efficiently and cost-effectively than conventional processes.

Excursus I: Cryogenic separation - downscaling

In the range of 500 m^3_{STP}/h economic feasibility for the cryogenic separation is more compromised and the specific production chain for the LCO_2 is jeopardised compromising the total carbon footprint reduction of the process if the cryogenic integrated solution is not used. The technology available at the market is focused on the liquid separation of CO_2 or the use of the solid separation linked to the polishing. Solid separation is in general cheaper in terms of CAPEX and OPEX (operational expenditure) and several projects started implementation during 2022. In the lower range around 250 m^3_{STP}/h, the feasibility might be reached with the solid cryogenic integration and the marketing of both products (bio-LNG and LCO_2). For a lower flow between 100 m^3_{STP}/h and 50 m^3_{STP}/h the cryogenic solution requires the cleaning process for water and H_2S and other impurities to be integrated in the same process and not with dedicated H_2S scrubbing equipment. This way, economic feasibility might be reached for these low-capacity facilities.

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The emerging market of bio-LNG production with parallel CO_2 valorisation in Europe is briefly presented in Excursus 2 below.

Excursus 2: bio-LNG production and CO_2 valorisation in Europe

Purified biomethane (purity 99.9 %mol) at the temperatures between −162 and −124 °C and pressures between 1 and 10 bar becomes liquid (referred to as biological liquefied natural gas or bio-LNG) and can be used as an alternative to Liquefied Natural Gas (LNG). The energy density of bio-LNG makes up for 60 % of energy density of diesel fuel. In comparison to the gaseous state of biomethane under normal conditions though, it is almost 600 times higher and 2 to 3 times higher than that of Compressed Natural Gas (CNG) or compressed biomethane (bio-CNG). This fact results in more profitable sales of bio-LNG compared to the gaseous biomethane, which is in particular relevant for the narrow biomethane production, and allows for the use of bio-LNG in maritime and heavy road transport sector (Capra et al., 2019).

As of the end of 2021, 15 European bio-LNG production facilities were in operation in Belgium, Denmark, Finland, France, Germany, Italy, the Netherlands, Norway, Sweden, and the UK. According to the envisaged production capacities by 2025, it is expected that Germany, Italy, and the Netherlands will be leading in bio-LNG production in Europe. There is an emerging market for CO_2 valorisation after biogas upgrading at bio-LNG plants. From 85 announced bio-LNG plants for the years 2022-2025, 32 are to expect to valorise their biogenic CO_2 stream (European Biogas Association, 2022b).

With respect to the cost assessment, the capture of CO_2, as well as the removal of impurities, is usually done for the upgrading of biomethane, which can be fed into the gas grid. In this manner, the capture of CO_2 is often seen as neutral in terms of costs in case the costs are assigned to the methane production (Rodin et al., 2020). However, as CO_2 capture provides another product in addition to biomethane production, the costs can be split accordingly. Finally, in the overall evaluation, the total costs are to be assessed in relation to the total revenues from all products provided. Moreover, the installation of a CO_2 capture unit requires, obviously, investments. The specific amounts of investments differ at country level and are indicated, where available, in section 3.4 below, partially in combination with further retrofitting measures. On a broader scale, from the macroeconomic point of view and taking social cost and value to the society into account, the production of (food-grade) CO_2 can be seen as a positive externality of biomethane production within the assessment of decarbonisation pathways (Liebetrau et al., 2022). In the context of fossil-based CO_2 shortages, high cost of natural gas can make the capture of biogenic CO_2 from biogas upgrading competitive. The average utilisable CO_2 capture potential from AD is equivalent to 6,000 t CO_2 per year and site (Rodin et al., 2020), which varies typically depending on country and specific production site and is admittedly lower in comparison to fossil-based CO_2 amounts per production unit, but allows for small-scale and decentralised CO_2 production facilities. In combination with decentralised points of sustainable sources of, for instance, H_2 and N_2 as described below in section 3.1.5, it enables creation of new sustainable business models.

The specific costs of CO_2 capture from different industrial processes are depicted in Figure 5. The depiction is based on the values provided by Rodin et al., 2020 differentiated by the biogenic, natural and fossil sources of CO_2. Thereby, the most conservative values were chosen in order to illustrate the specific cost ranges. In accordance with that, the costs of provision of biogenic CO_2 from biogas upgrading in the range 0 – 90 EUR/t can compete with the production cost of CO_2 from fossil sources.

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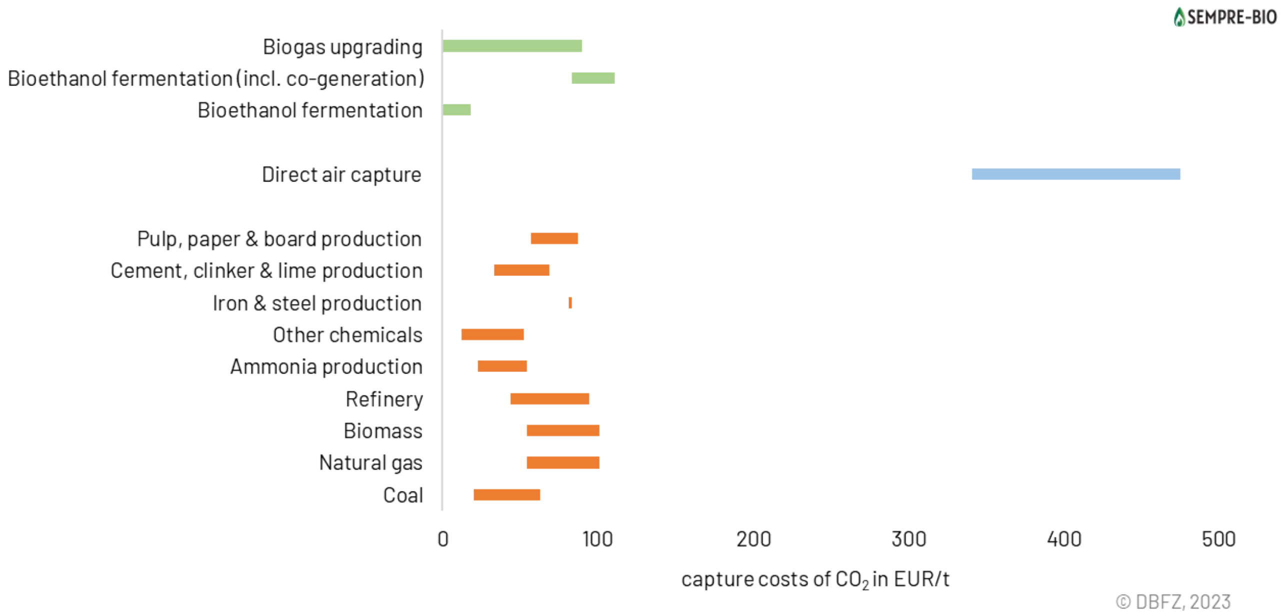

Figure 5: Ranges for the production cost of CO_2 from various industrial sectors, differentiated by the biogenic, natural, and fossil sources of CO_2 (source: own illustration based on Rodin et al., 2020)

1.4. CO_2 sources and prices in Europe

The current biogenic, natural and fossil sources of CO_2 for industrial utilisation in Europe are presented in Figure 6. According to that, almost the half of CO_2 in Europe is currently supplied by the synthesis of ammonia (48 %), followed by CO_2 from refineries and chemical industry (19 %), bioethanol production (16%), and natural wells (12 %). Hydrogen and combustion processes as sources for CO_2 in Europe play a minor role (5 % in total).

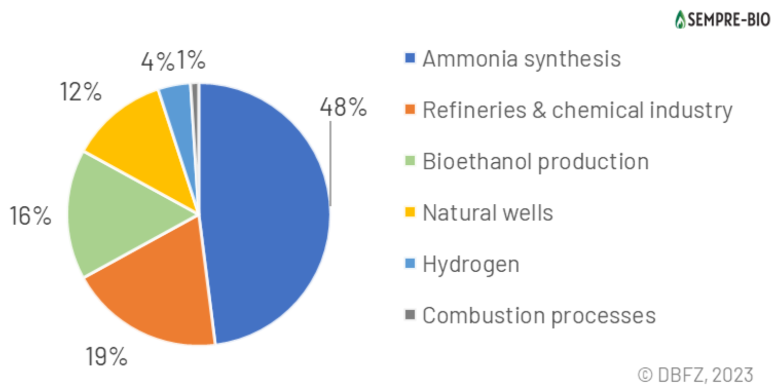

Figure 6: The current biogenic, natural and fossil sources providing CO_2 for industrial utilisation in Europe, relative share by weight (source: own illustration based on Pentair, 2018)

Therefore, the price of (fossil) CO_2 is subject to the cost of natural gas in case of fossil-based fertiliser production and distance to CO_2 production site (transport by road by truck meaning empty return in order to avoid contamination of CO_2 tanks by impurities/ other gases resulting from different demanded gas qualities) (Primer, 2022), the resulting regionality of the sourcing of CO_2 as well as the seasonality of the demand for CO_2, followed by the very long transport distances making transport costs prohibitive.

In 2022, the shortage on CO_2 was reported for some European countries, such as the United Kingdom, Italy, Poland or France (Reuters, 2022a; Ecquologia, 2022). The reasons for that are of a similar nature, first of all due to cutting of the CO_2 production by some major fertiliser producers in the United Kingdom, Norway and Germany due to the increase in energy costs. In addition, transport difficulties and the exceptionally hot weather in summer months can be named (ibid.). As the reaction, the food and

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beverage industry for instance in the United Kingdom appealed to the government to develop contingency plans in order to ensure CO_2 supplies (Reuters, 2022b).

The volatility of (fossil) CO_2 prices was reported across Europe. In the United Kingdom, in comparison to £200/t CO_2 in 2021 the prices spike over £1,000 t CO_2 up to £4,500 per t CO_2 were observed in 2022 (The Guardian, 2022). In France, before 2022 CO_2 price was reported to be around EUR 50-200/t CO_2, with an average of around EUR 120-150/t CO_2 for regular consumers not far from production sources (GRDF, 2023). However, it can be expected that CO_2 commodity prices will ease in the mid- and long-term.

In case of the provision of biogenic CO_2, biogas or biomethane plant size and CO_2 capture capacity (economies of scale resulting in the cost degression) as well as the seasonality and regionality are important factors governing the price of biogenic CO_2 making it competitive especially in the light of the elevated natural gas prices. Europewide, the price of biogenic CO_2 derived from anaerobic digestion was calculated to be 200 EUR/t without the price premium for its biogenic origin (Alberici et al., 2023).

2. Methodology of data collection

In the following, the process of data collection is described in accordance with the criteria applied during the literature review and the conducted surveys in order to collect relevant information on biogas and biomethane plants with CO_2 valorisation both in operation and in the planning stage in Europe.

2.1. Literature review

In order to collect relevant information on biogas and biomethane plants with CO_2 valorisation in Europe, different information sources such as research papers, European and national project results, technical reports, presentation slides, case studies, company websites, references of plant manufacturers, official documents relevant for the admission procedure of biomethane plants, permission requests, notifications of permission, and press articles were consulted between November 2022 and October 2023. For the collection of the scientific papers, the database Scopus was used. Thereby, the keyword was "*CO_2 valorisation*" and the focus on commercial-scale CCU projects without further consideration of possible CCS developments. Due to the high number of hits, the most recent and relevant papers were selected based on their actuality and relevance of the topics. For the identification of biomethane plants with CO_2 valorisation, after the consulting project results and technical reports general research was conducted using the keyword "*CO_2 valorisation*" or "*CO_2* and *biomethane*" in combination with the respective country name such as France, Norway, Italy, the Netherlands, the United Kingdom, and Germany, also in the respective original language.

An additional challenging aspect was that information on CO_2 valorisation (specific types and capture capacities) is in some cases not available through direct online research, possibly due to sensitivity issues, competition reasons, or can change from the previously announced to the actual sectors and amounts in use. The sources obtained in the course of the literature review are listed within the literature section. For the depictions in section 3.4 in form of a summarised overview of biogas and biomethane plants with CO_2 valorisation in Europe, the literature sources are summarised and denoted as DBFZ literature review, 2023. A precise attribution of the literature sources differentiated by the status of the biogas and biomethane plants with CO_2 valorisation in Europe (in operation vs. in the planning stage) can be found in Table 4 in Annex.

2.2. Survey

In the first step, the semi-standardised questionnaire (see Annex, questionnaire 1) with the survey on innovative plants, legal frameworks, barriers, and perspectives of biomethane production and utilisation in Europe was sent by email by DBFZ to the project partners of SEMPRE-BIO in February 2023. The aim of the questionnaire was among others to gather the information on the status quo of biomethane plants with CO_2 valorisation both in operation and in the planning stage in Europe (CCU projects) for those involved into the project countries. The inquired information entails

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- biomethane plant site,
- status (in operation resp. in the planning stage),
- year of initial/ planned operation of CO_2 capture unit,
- upgrading capacity and technology,
- substrates,
- CO_2 production per facility, and
- CO_2 utilisation sector.

After a small adaptation, the semi-standardised questionnaire (see Annex, questionnaire 2) was sent by DBFZ to the project partners of 3 further under Horizon Europe funded biomethane projects BIOMETHAVERSE (http://www.biomethaverse.eu/), HYFUELUP (https://hyfuelup.eu/), and METHAREN (https://metharen.eu/) in the second step in April 2023. In this way, all project partner countries involved into the SEMPRE-BIO and 3 further under Horizon Europe funded projects (Belgium, Denmark, France, Germany, Greece, Italy, Norway, Portugal, Spain, Sweden, Switzerland, the Netherlands, the United Kingdom, and Ukraine) were addressed as part of the survey. The survey responses were received by email. In addition, external to the SEMPRE-BIO project stakeholders in the area of biomethane from the Netherlands, Poland, and the United Kingdom were also written to and have received the questionnaire. The required information on valorisation of CO_2 from biogas and biomethane within the survey was classified by some stakeholders as sensitive and could not be provided. Therefore, not all countries could be covered by the survey but were covered by the literature review as described above in the section 2.1.

An overview of the projects, partner countries involved, and the number and type of institutions participated in the survey can be found in Table 1 below. In total, 18 experts from 12 institutions and 7 countries took part in the survey.

Table 1: Survey responses by representatives of the EU biomethane projects as of 06/2023 (source: DBFZ survey of 4 Horizon Europe projects on biomethane, 2023)

Project	Partner country	Number of respondent organisations	Acronym of respondent organisation	Type of respondent organisation
BIOMETHAVERSE	Italy	1	CIC	association
	Sweden	2	Energigas, RISE	association, research
	Ukraine	1	UABio	association
METHAREN	Italy	2	ACEA, Envipark	Industry, research and consulting
HYFUELUP	Portugal	1	BIOREF	Research and consulting
SEMPRE-BIO	Spain	3	CET, INV, UVIC	Research and consulting, consulting, academia
	Belgium	1	Biogas-E	association
	Denmark	1	DTU	academia

Further, DBFZ has conducted the annual survey of biomethane plant operators in Germany from February to May 2023 for the reference year 2022. For the survey, the semi-standardised questionnaire was used to collect relevant parameters for the plant operation but also information on actual and planned biogenic CO_2 valorisation. In total, 248 biomethane plant operators (both in operation and in the planning stage) were contacted. The response rate was 13 % which corresponds also to around 13 % of the total number of biomethane plants being in operation in Germany by the end of 2022. The overview of the sample and response rate is shown in Table 2 below.

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Table 2: Number of questionnaires sent and response rate within the framework of the survey of the German biomethane plant operators carried out by DBFZ as of 06/2023 (source: DBFZ survey of the German biomethane plant operators, 2023)

	Number of questionnaires sent, (n)	Number of responses received, (n)	Response rate, (%)
Survey biogas upgrading plants 2023, (year of reference 2022)	248	32	13

Along with the results of the literature review, as described in section 2.1 above, the findings from the surveys are introduced in section 3.3 in form of a summarised overview of biogas and biomethane plants with CO_2 valorisation in Europe, whereas in section 3.4 the selected projects examples for different countries are presented. Based on the collected data sample from both literature research and the conducted survey, the following depictions do not claim to be exhaustive but provide an insight into the currently very dynamic market situation.

3. CO_2 valorisation in Europe

This section delivers an overview of the different sectors for valorisation of biogenic CO_2, the results of surveys and literature research conducted by DBFZ, the selected project examples of valorisation of CO_2 from biogas and biomethane in European countries, followed by the summary of future opportunities of biogenic CO_2 valorisation.

3.1. Options of CO_2 valorisation: an overview

There are different CO_2 valorisation routes ranging from the well-established to those still to be explored (Rodin et al., 2020). Whereas the production of urea via Bosch-Meiser process, methanol via catalytic CO_2 hydrogenation, methane via CO_2 methanation, concrete curing, CO_2-derived polycarbonates and polyols represent mature technologies (technology readiness level TRL 8-9) (Chauvy and De Weireld, 2020), other innovative technologies such as production of biopolymers, biochemicals and alternative sources of protein from biogenic CO_2 to be demonstrated in SEMPRE-BIO by UVIC are from TRL 5 to TRL 7. An overview of the options for valorisation of biogenic CO_2 is shown in Table 3, whereas the selected options will be presented in detail in the sections 3.1.1 to 3.1.5 below based on their relevance for the SEMPRE-BIO project and the focus set on CCU pathways.

Table 3: Options of biogenic CO_2 valorisation (Sources: IEA Bioenergy Task 37, 2020; Kapoor et al., 2020; EIGA, 2020a; Podder et al., 2023)

Sector	Possible Applications
Agriculture	• Air enrichment in greenhouses • Insect pest control
Algaculture	• Algae production
Energy production	• Power-to-Gas • E-fuels • Algae biomass to biogas or biodiesel
Food and beverage industry	• Cooling food (i.e., modified atmosphere packing) • Carbonation of mineral waters and soda • Wine and beer production • Food processing (chilling, temperature controlling freezing, pH control)

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	• Stunning animals before slaughtering • Supercritical CO_2 as solvent for decaffeination of coffee beans, for production of flavours and essential oils
Building industry	• Cement • Concrete • Aggregates (filling materials)
Chemical industry	• Production of urea, methanol, dimethyl ether (DME) • Production of building blocks for biopolymers manufacturing (PHA/PHB)
Iron & machine industry	• Laser cutting • Welding in black steel • Shielding gas
Healthcare sector	• Laparoscopy (surgical procedure) • Dry ice for sending samples • Cooling eggs and sperm in fertility clinics
Pharmaceutical industry	• pH control • Dry ice for the transport of stem cells • Controlling oxygen levels in cell culture
Other	• Fire extinguishers • R744 (CO_2-based refrigerant) used in air conditioning systems • Industrial cleaning (solvent-free)

Various CCU pathways are characterised by different CO_2 sequestration periods such as long-term (centuries to millennia) versus short- (days, weeks, and months) and medium-term (decades). In addition, there is a different probability of release of CO_2 sequestered in the CO_2-based products (high versus low). In order to allow for CO_2 to be captured in stable products in the long term, it is required that such products are not changed or modified during their use and product lifetime. In the medium term, CO_2 stored in the products will be released on purpose or naturally by separation into initial components. In the short-term, the release of CO_2 happens immediately or shortly after the use of CO_2-based products, which is considered as a single reuse process of CO_2. In this case, especially relevant for CO_2 emissions reduction is the displacement of CO_2-intensive and fossil-based products by those based on biogenic CO_2 as well as the energy and resource intensity of the specific production process (Hepburn et al., 2019; ZEP, 2017).

The duration of storage of CO_2 for selected CCU pathways depending on the likelihood of CO_2 release can be found in Figure 7 (left). Accordingly, the shortest duration of CO_2 sequestration has CO_2-derived platform chemicals such as methanol or urea and CO_2-derived fuels such as methanol, methane and Fischer-Tropsch-derived fuels as well as microalgae-based biofuels, biomass, or bioproducts such as aquaculture feed. Among those not pictured with the short CO_2 sequestration are also CO_2 applications in the food and beverage industry and CO_2 for yield boosting in agriculture and algaculture.

The long-term CO_2 sequestration can be achieved by capturing CO_2 in building materials. Enhanced oil recovery (EOR) using CO_2 represents mature technology which essence is the injection of CO_2 into oil fields in order to enhance oil production. CO_2-EOR is primarily used in the United States and to a lower extent in Brazil, Canada, China and Turkey (IEA, 2019) and is not in the focus of this report. Another long-term CO_2 storage possibility is delivered by BECCS (geological storage with bio-CCS). Further, paths for mid-term CO_2 sequestration that are not yet depicted but must be named such as biochar gained in the course of biomass pyrolysis and soil and forest (afforestation, reforestation or sustainable forest management) carbon sequestration (Hepburn et al., 2019). These paths are, however, also beyond the scope of this report.

When projecting the utilisation potential of CO_2 for selected CCU pathways by 2050, the production of fuels with 1,000 to 4,200 Mt CO_2 utilised per year has the highest valorisation potential by volume (Hepburn et al., 2019), which is also in line with the assessment by IEA, 2019. In contrast, chemical production is seen as the lowest CO_2 valorisation pathway by volume with 300 to 600 Mt CO_2 by 2050 (Hepburn et al., 2019). The utilisation potential of CO_2 in Mt CO_2 valorised per year for selected CCU pathways by 2050 is shown in Figure 7 (right).

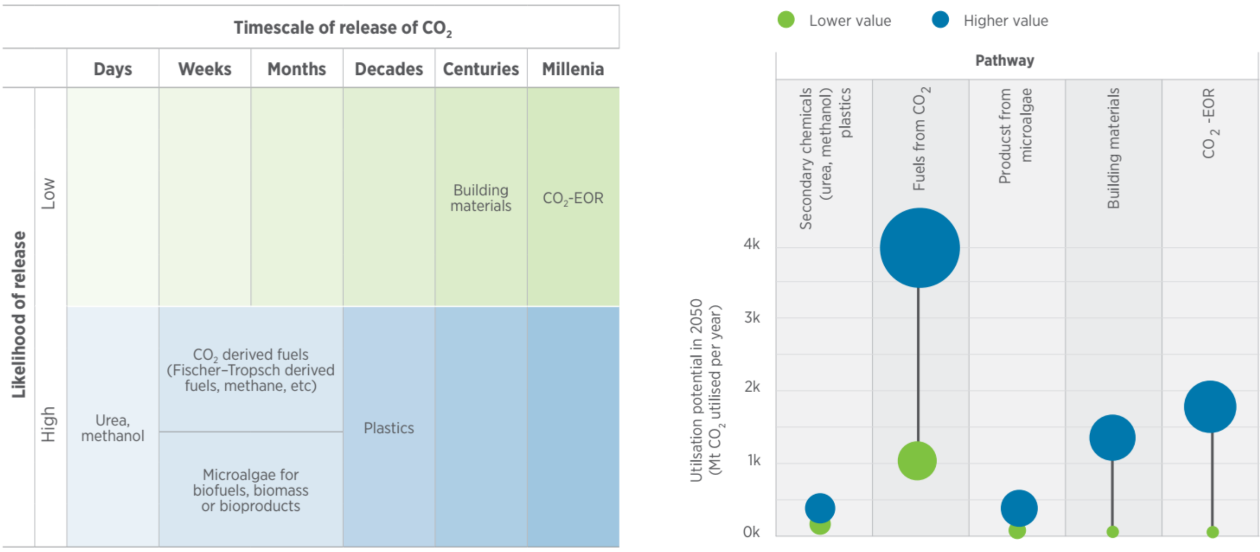

Figure 7: Permanence of storage of CO_2 for selected CCU pathways versus likelihood of CO_2 release (high/low) (left); Range estimates of the potential for CO_2 utilisation in 2050 (Mt CO_2 utilised per year) (right); CO_2-EOR = enhanced oil recovery using CO_2 (source: Lyons et al., 2021 based on Hepburn et al., 2019)

3.1.1. Agriculture

CO_2 air enrichment in greenhouses

In greenhouses, the productivity is dependent on internal CO_2 concentration, temperature, and solar radiation. In comparison to the atmospheric CO_2 concentration of around 410 ppm, indoor CO_2 concentration rates between 600 and 1,000 ppm in greenhouses have been proven to increase photosynthesis and therefore the yields typically by 20 – 30. The use of CO_2 in greenhouses represents state-of-the-art application and depends, among others, on the specific dosage requirements for different crops, scale and design of greenhouse, and price of CO_2. Depending on the different times of the day and the season, masses of CO_2 uptake by horticultural crops and CO_2 indoor concentrations can vary. The supplied average rates are between 100 and 300 kg CO_2 /ha/h. A typical 5 ha greenhouse requires 460 t CO_2 per ha annually rates (van Tuyll et al., 2022). There is higher demand of CO_2 in summer months due to the higher crop growth rate but also greater losses of CO_2 as a result of higher ventilation rates (van Tuyll et al., 2022; Oreggioni et al., 2019). In case of CO_2 enrichment of greenhouses compared to other CO_2 valorisation paths, a lower energy demand for conversion of CO_2 into a final product is especially beneficial. From the environmental point of view, biogenic CO_2 can replace fossil fuels (mainly natural gas) which would be burned instead in combined heat and power (CHP) installations or boilers in order to generate the needed heat and CO_2 off-gas for the enrichment. This will avoid further GHG emissions. This is especially relevant for the summer, when natural gas is burned in order to generate

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CO_2 but leading to the unnecessary heat production (van Tuyll et al., 2022; Oreggioni et al., 2019; Kapoor et al., 2020).

In some countries, such as the Netherlands, CO_2 for horticulture can be supplied via pipeline (by the Dutch company OCAP (Organic Carbondioxide for Assimilation of Plants) CO_2 B.V. from 2 petrochemical sites) which requires a higher investment but has lower variable costs. In other cases, especially in decentralised greenhouses, the supply by trucks with the capacity of 20-25 t liquid CO_2 is common. In this case, costs for the transportation and quality control check of CO_2 are of importance. Taking the market competitiveness into account, the total costs for liquid biogenic CO_2 from biomethane plants for instance in the Netherlands were identified to vary between 55 and 105 €/t of delivered CO_2, whereas the purchase costs of liquid CO_2 from chemical producer could be amounted to 80-150 € per tonne of CO_2 depending on distance and capacity (Mikunda et al., 2015; van Tuyll et al., 2022). Cost reduction potential could be provided by the matching the locations of the greenhouses to the existing and future biomethane or in case of pipelines the upgrading plants in order to identify the cost-optimal CO_2 supply routes in combination with the possible heat supply which would result in more stable prices contrary to the prices for natural gas. Another option could be provided by merging biogas from different producers to one biomethane upgrading facility (already existing such as in Bitburg in Germany for biogas merging) which would enable economies for scale for both biomethane production and CO_2 recovery and in parallel reduce the transportation costs while providing opportunities to green label the used biogenic CO_2 (Mikunda et al., 2015).

If using liquid biogenic CO_2 which would represent an external source especially allowing to meet the peak demand, the storage tanks can be placed outside of the greenhouse enabling the spraying of CO_2 via vaporiser inside the greenhouse (Kapoor et al., 2020). If using CO_2 in greenhouses via spraying in order to speed up the photosynthesis rate, the food quality of CO_2 is not required, although bottled CO_2 is usually food-grade and higher purity grades might be required for specific crops. Besides, there are specific purity requirements for CO_2 transported via pipeline too. Although biogas upgrading provides one of the purest CO_2 in comparison to CO_2 from other sources, the impurities such as NH_3 and VOCs might still occur and H_2S in concentration less than 0.02 wt% can be toxic to the crops and workers. Therefor, the biogenic CO_2 flow from biomethane production will likely be free of the main contaminants NO_x, ethylene and SO_2, which might be phytotoxic, resulting from the combustion (Mikunda et al., 2015; van Tuyll et al., 2022; Kapoor et al., 2020). In general, the enrichment of greenhouses with CO_2 can lead to CO_2 recovery rates of 14 – 67 % (Oreggioni et al., 2019).

Insect pest control

For insect pest management in granaries and warehouses, chemical fumigants such as carbon tetrachloride, ethylene dibromide, aluminium phosphide, sodium cyanide were used to control insect pests in the stored goods. Later on, they were replaced by phosphine and methyl bromide. The latter was banned in 2015 as one of the causes of ozone depletion. Phosphine is still applied in grain storage due to its cheapness. However, the pest resistance against phosphine, potential residues in the stored products that might be even carcinogenic to humans, and corrosion of metallic storage surface were identified as the reasons for the search for alternatives. As a chemical substitute to phosphine, cost-intensive, potentially GHG causing and insect-tolerant sulfuryl fluoride and hydrogen cyanide can act (Kumar et al., 2022). CO_2 represents a biogenic alternative, since it is not hazardous and simple to apply, acts fast and leaves no chemical residues in the products, while being effective in all stages of insects' growth cycle and disappearing after the aeration. It is of importance to care for working safety during the application. The research on the controlled atmosphere, where the atmospheric composition is controlled at the duration and level mortal to the pests, was carried out for more than 40 years and represents a well-established method (Navarro et al., 2012). Liquid CO_2 can be added via pressurised cylinders to a sealed, gas-tight silo changing to gas form after being released in controlled amounts through vaporiser with the minimum concentration of 35 % CO_2 (Kapoor et al., 2020) under normal atmospheric pressure (Navarro et al., 2012). The required exposure duration to the elevated CO_2 levels is

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14-15 days at the temperature ≥ 20 ºC (Kumar et al., 2022; Kapoor et al., 2020). Controlled atmosphere with CO_2 concentrations of 60 % results in 95 % control of most insects (Navarro et al., 2012) in four days at the temperature of 28 ºC (Kumar et al., 2022). The use of high-pressured CO_2 (10-37 bar) can significantly reduce the exposure time to hours in metallic chambers standing the high pressures. However, this solution requires high capital investment and is therefore recommended for high-value commodities such as nuts, medicinal herbs, spices etc. (Kumar et al., 2022; Navarro et al., 2012). The commercial use of modified or controlled atmosphere is especially relevant for organic products for which no chemical fumigants are allowed (Navarro et al., 2012). In the lab tests, the use of biogenic CO_2 with the traces of CH_4 and H_2S derived from biogas plants demonstrated higher efficacy in insect mortality compared to pure CO_2 (Kumar et al., 2022). However, in this case special attention should be paid to occupational health and safety.

3.1.2. Algae production

Algae represent sustainable future microbial cell factories which convert CO_2 to biomass via photosynthesis with a great potential in generating high value-added products. They are divided into two sub-groups such as macro- (known as seaweed) and microalgae (referred to as phytoplankton). In comparison to macroalgae, microalgae have a faster and more uniform growth pattern and are more economically sustainable (De et al., 2023). The specific competitive advantage of microalgae cultivation systems lies in the aforementioned wide application potential resulting from the rate of biomass production, high efficiency of photochemical processes, genetic diversity, resistance to harsh environmental conditions, especially in comparison to land plants, and capability to metabolise many pollutants. Due to its ability to fix CO_2, microalgae cultivation represents an auspicious CCU option (Zieliński et al., 2023). Algae are cultivated in open systems such as natural waters and artificial (raceway and circular) ponds. In addition, there are closed cultivation systems such as tubular, vertical column, and flat panel photobioreactors (Alami et al., 2021). To a lesser extent, for algae cultivation fermenters are also used representing a more recently developed method (Araújo et al., 2021). The capture efficiency of CO_2 is dependent on the concentration of CO_2, the selected algae strain, cultivation system, and environmental and operating conditions, especially available light and light penetration in the water system. The specific capture efficiencies of CO_2 by algae can achieve 80 to 99 % under favourable conditions (Alami et al., 2021), although the current practical efficiency is lower compared to other CO_2 capture technologies (Zieliński et al., 2023). However, this is not the relevant efficiency factor. More important is the energy efficiency. For algae production, pure CO_2 is not needed and can be sourced from different flue gases. This saves energy and technical processes, which are required for CO_2 concentration for other processes. Moreover, natural sunlight is often used as the main energy source for CO_2 recovery, added by some electricity for pumping or integration of CO_2 into the water. However, the specific composition of flue gases is of importance. Whereas compounds such as NO can be metabolised (Alami et al., 2021) at low concentrations, SO_2 in concentration above 60 ppm (Zieliński et al., 2023) can be toxic to algae. CO_2 flow rates are also relevant, since very high flow rates can inhibit the growth and production of algal biomass (Alami et al., 2021). Algae have an additional effect on de-eutrophication and some microalgae can be used for phycoremediation of degraded water bodies removing or converting toxic and resistant pollutants. The oxygen excretion from photosynthesis into the water body enhances the redox potential and leads to lower levels of biogenic compounds in and better quality of water. Heterotrophic microalgae do additional direct consumption of organic pollutants. For their cultivation, liquid residual effluents and wastewater as well as the water from natural bodies with high biogenic share can be used as the culture medium, while the pesticides or herbicides are not necessarily required (Zieliński et al., 2023).

In Europe, the most microalgae production facilities are located in Germany, France and Spain. Together with Italy, these countries have the largest number of *Spirulina spp.* production sites with France dominating the production. Thereby, photobioreactors represent the most commonly used method of microalgae cultivation in Europe. The main application areas of microalgae biomass are food supplements and nutraceuticals with 24 %, cosmetics with 24 %, and feed with 19 % contributing

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together to 67 % of the total uses based on the shares of commercial biomass applications by production companies (Araújo et al., 2021).

Further production routes from microalgae involve hydrogen recovery or dark fermentation with methane, biodiesel production from storage lipids, fermentation to bioethanol, acetone and butanol, biohydrogen production via biophotolysis, bio-oil production via pyrolysis and hydrothermal liquefaction, and biochar production via pyrolysis. The long-term CCU option includes use of microalgae as biostimulants in place of synthetic liquid fertilisers in order to improve crop production while providing an economical and sustainable solution for organic agriculture. Microalgae can be further used to produce biodegradable bioplastics via CO_2 biosequestration which could be utilised for medical purposes such as production of wound dressings, manufacture of implants, and drug delivery carriers. In addition, via precipitation of $CaCO_3$ by blue-green algae, and non-phototrophic bacteria microalgae can be used for cement production (Zieliński et al., 2023).

The integration of microalgae cultivation systems into biogas (upgrading) plants or wastewater treatment plants offers the opportunity to harness biogenic CO_2 and a growth medium with the right amount and quality of nutrients, including biogenic compounds, for the production of value-added products while enabling the utilisation of waste heat (ibid.). The future-oriented options for the production of single cell proteins on the basis of microalgae cultivation using CO_2 from biogas production, along with insights into the production and cost framework, are envisaged in the project SEMPRE-BIO and described, among others, in more detail in section 3.2.

3.1.3. Food and beverage industry

For the use in the food and beverage industry, very high purity of CO_2 is required. The most used application of CO_2 in the world is the carbonation of mineral waters and soda (Girardon, 2019), followed by the production of de-oxygenated water, beer, and (sparkling) wine which require great amounts of CO_2 for their production (Zhang et al., 2020). Representing a weak acidifying agent, CO_2 can control the pH of milk or drinking water by lowering the hardness of the latter in place of strong acids such as sulfuric acid which is difficult to handle. CO_2 as compacted dry ice at the temperature -78 ºC is used for controlling the cold chain in the course of industrial processes and logistics or chilling of food products. However, for this type of use sophisticated facilities are required (Girardon, 2019). Dry ice can be further used for dry ice blasting when solid form of CO_2 is used as cleaning medium in the food and beverage processing and packaging industries. It represents environmentally friendly, nonabrasive, nontoxic, and dry technique leaving no residues or secondary waste. By removing protein residues on food-processing units, dry ice can minimise cross-contamination induced by allergens such as nuts or the like. In addition, it can also minimise contamination on surfaces by *Listeria*, *Salmonella* and *E. coli* (Vansant, Rogiers, 2019).

In case of freeze drying or dehydration, liquid CO_2, dry ice, and modified atmosphere packaging (MAP) techniques are applied for refrigeration. The temporary storage for all CCU is justified if the source of CO_2 is of biogenic nature (Zhang et al., 2020). Due to its fungistatic and bacteriostatic properties, CO_2 can minimise the increase of mould and bacteria especially in the absence of oxygen. Therefore, it is applied in the modified atmosphere packaging (MAP) process for perishable foods such as fish, meat, vegetables, and ready-made meals. It is injected into the package in order to decelerate the oxidation rate being effective at concentration > 20 % (Girardon, 2019; Kapoor et al., 2020).

Further, CO_2 can be converted into a supercritical fluid in order to extract various bioactive natural compounds. The desired critical stage is achieved when enhancing the temperature and pressure above its critical points (31.1 ºC and 7.4 MPa). The benefits are seen in its inexpensive nature, low reaction conditions, and non-flammability but also in easier product recovery, solvent-free extraction, and possibility to re-use CO_2. Supercritical CO_2 can be used as a solvent for decaffeination of coffee beans or removal of pesticides from harvested crops. It is also used in order to extract nutraceuticals, flavours and essential oils (e.g., ginger oil and oleoresin from ginger rhizomes with the latter being used food and pharmaceutical industries, patchouli essential oil, almond oil, cherry seed oil, Cannabis oil) or fatty acids

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and lipids from various feedstocks, as, for instance, eicosapentaenoic acid and docosahexaenoic acid from microalgae *Nannochloropsis* sp. instead of fish oil (Podder et al., 2023).

In Excursus 3, requirements for the food quality standards of CO_2 are described in detail. In addition to its use in the food and beverage industry, food-grade CO2 can be also used in the other industrial applications in order to avoid contamination of CO2 tanks by impurities or other gases resulting from different demanded gas qualities while being transported to the different end users.

Excursus 3: Requirements for the food quality standards of CO_2

For specific CO_2 uses, especially for, but also not limited to food and beverage industry, there are concrete standards of CO_2 required. This type of safety standard is referred to as food-grade CO_2. Accordingly, CO_2 has to be purified, controlled and can be traded only under specific documentation, reporting and quality requirements.

CO_2 as foodstuff gas can be defined as gas which is suitable for use in foodstuffs and can act as *food additive*, *technical additive* or *protective gas*.

- *Food additive* is defined according to the Regulation (EC) No 1333/2008 as a substance, with or without nutritional value, which is not normally consumed as a food itself or used as a characteristic food ingredient and is added to a food for technological reasons during manufacture, processing, preparation, treatment, packaging, transport or storage (Industriegaseverband, 2018). In this case, CO_2 is labelled as E290.
- *Technical additive* is defined as a substance which is not consumed as food itself but is used in the processing of food and may remain in residual quantities in the final product in which it does not fulfil a technological purpose (ibid.).
- Lastly, *protective gas* is defined as gas filled into food packaging for the purpose of preservation (atmosphere exchange, oxygen displacement, germ-inhibiting effect) (ibid.).

At the company level of the food business operators, against the background of the Regulation (EC) No 852/2004 on the hygiene of foodstuffs, Article 5 there is a need to develop and implement an intern HACCP-(Hazard Analysis and Critical Control Point) concept in order to ensure the control and quality assurance of the food-grade CO_2 which calls for comprehensive documentation requirements (European Union, 2004). In addition, the manufacturing process should be described in detail – from receipt or production of the raw gas until the product is placed on the market (Industriegaseverband, 2018).

Excursus 3: Requirements for the food quality standards of CO_2 (continued)

HACCP can be seen as a part of the overall quality management system, i.e., Global Food Safety Initiative (GFSI) scheme FSSC 22000, Food Safety management systems or ISO 22000, Food Safety Management (EIGA, 2020a). *FSSC 22000* represents a complete certification scheme for food and feed safety management systems based on ISO 22000 providing a certification model which can be used in the whole food supply chain. It covers sectors with the realised technical specifications for sector requirements for prerequisite programmes (PRPs) (ibid.). In contrast to FSSC 22000, *ISO 22000* is based on ISO 9001 entailing requirements for food safety management systems and not containing specific requirements for prerequisite programmes but calling for internal appropriate programmes at the organisational level (ibid.).

For *food additive gases*, there are minimum specifications from the Joint FAO (Food and Agricultural Organisation of the United Nations) / WHO (World Health Organisation) Expert Committee on Food Additives (JECFA), whereas for technical additives and protective gases there are no specific purity criteria which would apply under the EU law (EIGA, 2020b).

Further, internationally accepted guidelines for food-grade CO_2 (specific thresholds for possible contaminants such as nitrogen oxides, ammonia, volatile hydrocarbons in combination with appropriate detection methods for these potential pollutants) are provided by the International Society of Beverage Technologists (ISBT) and the European Industrial Gases Association (EIGA) (ISBT, 2023; EIGA, 2020b; Esposito et al., 2019). Although ISBT operates in Europe, it has its origin in Northern America. Relevant for the European market are more EIGA standards.

With respect to the EIGA standards on food-grade CO_2 from anaerobic digestion, the document 70/17 Carbon Dioxide Food and Beverages Grade, Source Qualification, Quality Standards and Verification is of relevance (EIGA, 2017). The allowed type of sources for AD are energy crops and organic waste with the required detailed and extensive risk assessment and compliance of the final product with the appendix A of the EIGA document 70/17. Thereby, the food safety risk assessment includes the digester AD process (ibid.). The handling of CO_2 derived from energy crops is treated as equal to that from yeast-based fermentation (ethanol), whereas the gas from co-digestion or organic waste calls for greater care in evaluation.

For AD plants and feedstocks, a compliance with EU regulations EC 1069/2009 Regulation (EC) No 1069/2009 of the European Parliament and of the Council of 21 October 2009 is expected laying down health rules as regards animal by-products and derived products not intended for human consumption and repealing Regulation (EC) No 1774/2002 (Animal by-products Regulation) and EC 142/2011 (ibid.). Finally, before supply to customer there is an online analysis of the CO_2 production or complete batch analysis needed (ibid.).

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3.1.4. Power-to-X

Power-to-X (PtX) stands for the process of conversion of the excess renewable electricity into H_2 through electrochemical reaction and further on by reaction with carbon compounds to product 'X'. Thereby, depending on the type of product and PtX technologies, X is referred to: the power-to-gas (P2G), power-to-liquids (P2L), power-to-chemicals (P2C), power-to-hydrogen (P2H_2), power-to-methane (P2M) or power-to-heat (P2H) (Dahiru et al., 2022).

In addition, there are different terms depending on the application of the products. If fuels are provided by PtX technologies, the term electrofuels or e-fuels is used. If combining hydrogen with biogenic sources of CO_2, it is a matter of bio-electrofuels or bio-e-fuels (Grahn et al., 2022).

The additional provision of biomethane via methanation is described below, since this is a special application within the context of the current report. Power-to-Gas describes the process of conversion of renewable electricity in order to produce H_2 via electrolysis (P2H_2) which is used with CO_2 from an external source to convert CH_4 (or synthetic natural gas, SNG) through the methanation (P2M). Both hydrogen and methane can be injected into the natural gas grid for subsequent storage. For hydrogen, this injection is limited by technical and regulatory framework conditions, since adjustment of the natural gas grids to higher hydrogen blending requires investments and research (Sterner, Specht, 2021), whereas these restrictions do not apply for methane, thus allowing either for its direct use or (seasonal) storage (Thema et al., 2019). Compared to the direct use of electricity or H_2, the lower efficiency of the process proves to be a disadvantage. However, the generated CH_4 injected into the gas grid can be used for industry, transportation, and buildings (Sterner, Specht, 2021).

The first step is the production of hydrogen which can comprise water electrolysis where water is split into H_2 and O_2 representing mature technology. The energy needed for water electrolysis can be supplied by electrical or thermal energy and in case of the renewables such as wind or solar being used can potentially result in net-zero CO_2 emissions (Dahiru et al., 2022). Currently, alkaline and membrane electrolysis are available, whereas high-temperature electrolysis is under development (Sterner, Specht, 2021). Relevant for the selection of electrolysis technology are efficiency, lifetime, and flexibility (Dahiru et al., 2022). The second step is the process of the conversion of H_2 and CO_2 using electrical energy which is referred to as methanation and can be differentiated into thermochemical or catalytic methanation and biological methanation. For biological methanation, biological catalysts such as methanogenic microorganisms are used in order to catalyse the methanation reaction at the process temperatures between 37 and 65 °C and pressures 1-15 bars (Thema et al., 2019). In case of in-situ biological methanation, hydrogen is directly brought into the AD reactor, whereas in case of ex-situ, H_2 and CO_2 can react in a separate reactor filled with hydrogenotrophic archaea. In comparison to in-situ with 75 %, greater volumetric methane production rates of approx. 98 % can be realised in ex-situ (Dahiru et al., 2022). Of additional relevance for the gas production cost is the source and type of the feedstock utilised for biological methanation (Dahiru et al., 2022). For thermochemical methanation (Sabatier process, $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$), metal catalysts such as Ni/Al_2O_3 are used in order to catalyse the methanation reaction at the process temperatures between 200 and 550 °C depending on the optimal activity of the catalyst and pressures up to 100 bar (Thema et al., 2019).

The thermochemical methanation is distinguished by its high space-time yields and waste heat temperature level, less space needs, availability for high MW scale and proof for a long time. The biological methanation is characterised by less sensitivity to the gas impurities of the reactants and higher robustness, lower temperatures and pressures requirements and greater suitability for decentralised applications in particular if combining with biogas (Sterner, Specht, 2021).

The CO_2 intensity of the electricity mix (share of the renewables with the lower CO_2 intensity compared to the fossil sources within the electricity mix) is decisive for the PtX products. The biogenic or atmospheric sources of CO_2 are to be preferred to flue gases from the fossil power plants – in case of CO_2 from biogas not only from the sustainability point of view but also due to the lower energy demand which is needed to capture CO_2. For market uptake of PtX, OPEX funding, CO_2 pricing and quota system

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are possible support instruments (ibid.). According to the review of PtX projects in Europe carried out by Wulf et al., 2020, from 220 of the PtX projects commissioned after 2000 until 2020 (without being decommissioned afterwards) in 20 European countries with the TRL level ≥ 5 and CO_2 sourced from biogas or wastewater treatment plants, 8 are located in Germany, 3 in Denmark, 3 in Switzerland, and one project each in Spain, France and Italy. Where indicated, 64 % of these projects were based on biological methanation, whereas 36 % were represented by catalytic methanation (Wulf et al., 2020).

3.1.5. Chemical industry

Fertiliser industry

Mineral fertilisers, especially nitrogen (N) fertilisers, represent a necessary foundation of nutrient supply in agriculture in order to produce food, feed, fuel and/ or fibre. Ammonia is in turn the basis for chemical N-fertilisers with urea being a direct derivative of it. Among with agricultural use as fertiliser, urea (N= 46 %) serves also as an intermediate for production of resins or as a chemical agent in order to reduce NO_x emissions from power plants, engines and other exhaust gases. In comparison to other macronutrients such as phosphorus (P) and potassium (K), N-fertilisers are the most applied and most energy-intensive to manufacture (IEA, 2021). The specific amounts and application rates vary region- and crop-related though. Whereas globally in 2020, 112.4 Mt (nutrient-related) of N-fertilisers were consumed, 9.1 Mt were applied in the EU-27 in 2021/22. 49 % of these amounts (nutrient-based) were globally consumed in form of urea and 22 % in the EU-27 for agricultural use only. In 2022 in the EU-27, 7.4 Mt of N-fertiliser (nutrient-based) were consumed for agricultural and industrial use representing 46 % of the total EU-27 consumption (Fertilizers Europe, 2023a).

The synthesis of urea requires CO_2 (Driver et al., 2019). Usually, CO_2 accruing as a result of ammonium production with natural gas is used for urea synthesis. The use of fossil fuels results in approx. 250 Mt CO_2 (direct process CO_2 emissions) and around 130 Mt CO_2 are used directly to produce urea (Figure 8) and are released again along with N_2O emissions in the course of the urea application in agriculture. 130 Mt CO_2 correspond to around 29 % of the total generated CO_2 emissions during ammonia production (with 450 Mt CO_2 in total in 2020 representing the largest emitter in the chemical industry sector). The additional process energy input leads to diluted CO_2 flow which needs further facilities in order to be captured (IEA, 2021). The urea production units are typically located close to the natural gas production sites where steam reformation of methane generates a syngas consisting of hydrogen (H_2) and carbon monoxide (CO), which is upgraded to enhance the amount of H_2 and to produce CO_2. After removing the CO_2, in the course of the Haber-Bosch process H_2 reacts with N_2 from the air to produce ammonia (NH_3). The separated CO_2 reacts with NH_3 to generate ammonium carbamate ($H_2NCOONH_4$). Through the Bosch-Meiser process, $H_2NCOONH_4$ forms urea ($CO(NH_2)_2$) and water (Driver et al., 2019).

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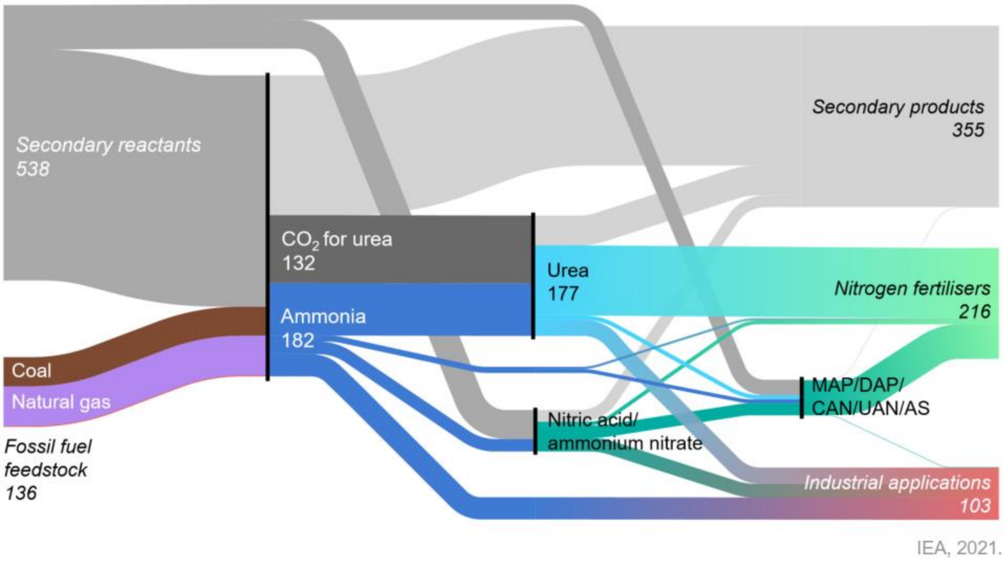

Figure 8: Mass flows in the ammonia supply chain from fossil fuel feedstocks to nitrogen fertilisers and industrial products, million tonnes per year of production using production data for 2019. Only the fossil fuel quantities consumed as feedstock are shown; the diagram does not represent process energy inputs. MAP = monoammonium phosphate; DAP = diammonium phosphate; CAN = calcium ammonium nitrate; UAN = urea ammonium nitrate; AS = ammonium sulphate (source: IEA, 2021)

Besides the use for urea synthesis, the CO_2 from ammonia production can be used after compression in the food and beverage industry or captured for geological storage (IEA, 2021). For urea production, about 0.74 tonnes CO_2 are used per tonne final product (Chauvy and De Weireld, 2020). Given the CO_2 shortages derived from reduced production of the fertiliser industry in 2022 and the envisaged decarbonisation efforts, as outlined in the section 1 above, the need for biogenic alternatives of CO_2 is expected to rise.

One possibility to decarbonise urea production is to substitute hydrogen from fossil sources (mainly natural gas, but also coal and oil) needed for ammonia production by hydrogen from more sustainable technologies. Depending on the colour scheme of hydrogen attributed depending on its specific production pathway, a distinction can be drawn between

- grey (conventional path),
- blue (conventional path combined with CO_2 capture from steam reforming process for CCS),
- green (based on renewables, mainly by electrolysis using renewable (like wind, solar, hydro, geothermal) electricity with H_2 being produced on site or supplied via pipeline),
- yellow (electrolysis using specific electricity mix from the grid depending on the production place and country), and
- turquoise (methane pyrolysis using specific electricity mix from the grid, technologically still to be further developed) ammonia.

Depending on the chosen scenario (base case vs. best case) and time horizon (2030 vs. 2050) with the geographical scope on the EU and Norway, turquoise, yellow, and green ammonia could result in 100 % CO_2 emissions reduction by 2050 in the course of the production, if the electricity grid will be decarbonised at this point. Turquoise ammonia cannot be achieved by 2030 but may have the development and decarbonisation potential in the long term, depending on the cost developments of the different routes. This will be dependent on the benchmark development of electrolysis H_2, which depends on the development of electrolysers costs, especially in case of operation with fluctuating electricity surpluses from wind and solar and on the development of available cheap renewable electricity, which in turn depends on the build-up of renewable electricity production, especially of wind and solar with relative low costs and times with low prices of such electricity on the markets. The costs for yellow ammonia are 2.8 times and CO_2 emissions almost by 40 % higher by 2030 compared to the grey ammonia. However, these values vary depending on the electricity mix and production site. Currently, the produced renewable energy could not meet the need to produce green hydrogen in order to convert the entire production sites to green ammonia. Blue ammonia represents bridge technology

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until scale-up of green or turquoise ammonia production. Crucial for blue ammonia is the location resp. vicinity of the possible storage sites, the transport infrastructure for CO_2 and the support from the politics and society. Since no CO_2 is generated in the production process of blue, green, yellow, and turquoise ammonia, an alternative source of CO_2 is required for subsequent urea production (Ausfelder et al., 2022).

Taking a more global perspective, where a lot of scenarios contain the import of green H_2 from regions with optimal renewable conditions, it is a question, if further NH_3 production in Europe makes sense and can be competitive in the long term, as NH_3 is in discussion as a distribution way for H_2 due to its much better characteristics (volume-related energy with relatively low pressure and temperature). Most probably, H_2 imports will be done via synthesised NH_3, CH_4 or other molecules with better storage and transport conditions than H_2.

Blue ammonia is, however, not to be equated with the *Blue Urea* concept, where the renewable-powered electrolysis to generate H_2 is combined with point-source CO_2 capture to produce urea via synthetic route (by generating ammonium carbamate precipitate which reacts to urea under less severe conditions (140 ºC, 14 bar) and with lower energy demand in comparison to conventional urea production path (170–220 ºC, 150 bar). Though being carried out under controlled conditions within a closed-system, *Blue Urea* concept might be reduced-carbon or even carbon-neutral and have several benefits if being upscaled. The production units could be more small-scale and decentralised close to the point of sources due to the sustainable origin of H_2, N_2 and CO_2. In addition, reduced transportation costs and the emissions compared to conventional production can be reported as well. In order to evaluate its overall performance, the concept should be tested in open air and uncontrolled conditions (Driver et al., 2019).

Possible changes by the import of renewable H_2 as ammonia, as described above, which can also be used directly for fertiliser production, may change the nitrogen fertiliser production within Europe strongly.

Methanol production

Methanol (CH_3OH) represents water-soluble, readily biodegradable, liquid chemical and clean-burning, biodegradable fuel. It is an energy carrier in electricity, automotive, and marine sectors as well as a rising renewable energy source (Methanol Institute, 2023). Synthesis of methanol relies mainly on fossil fuels: to 65 % on natural gas, to 35 % on coal (primarily in China) and to about 0.2 % on biomass and renewables (IRENA and Methanol Institute, 2021). The commercial production of methanol is based on the syngas synthesis from natural gas. The process includes two steps: steam reforming of methane and methanol production. Steam reforming of methane results in a mixture of CO, CO_2 and H_2. The production of CO_2 can also result from water-gas shift reaction which is used in order to modulate the ratio of H_2 and CO_2 for methanol synthesis. Steam reforming is the costly production part which requires very high temperatures and pressure (approx. 900 ºC and 16-30 bar respectively) (Azhari et al., 2022). In order to produce on average 2,500 tonnes of methanol per day in a conventional plant, temperatures and pressure of 200-300 ºC and 35-54 bar on the catalyst $CuO/ZnO/Al_2O_3$ are required ($CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$) (Sheppard et al., 2022). The last step comprises distillation of crude methanol in order to remove the water generated during methanol synthesis as well as possible by-products (IRENA and Methanol Institute, 2021). The generated water can be reused by water-gas shift reaction. Whereas steam methane reforming results in 0.7 t of CO_2 per tonne of methanol, coal gasification leads to 2.971 t of CO_2 emissions per tonne final product (Sheppard et al., 2023). In total in 2020, methanol production contributed 220 Mt CO_2 emissions in the chemical sector (IEA, 2021). Renewable methanol is the term used for methanol production based on renewable energy and renewable feedstocks containing carbon. Bio-methanol is produced from biomass such as agricultural and forestry waste and by-products, biogas from landfill, sewage, municipal solid waste, black liquor from the pulp and paper industry. The production of green e-methanol relies on green hydrogen (produced via water electrolysis using renewables) and CO_2 from renewable sources, such as BECCS or DAC (IRENA and Methanol Institute,

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2021) and is referred to as catalytic CO_2 hydrogenation (Azhari et al., 2022). The different production pathways of methanol are shown in Figure 9.

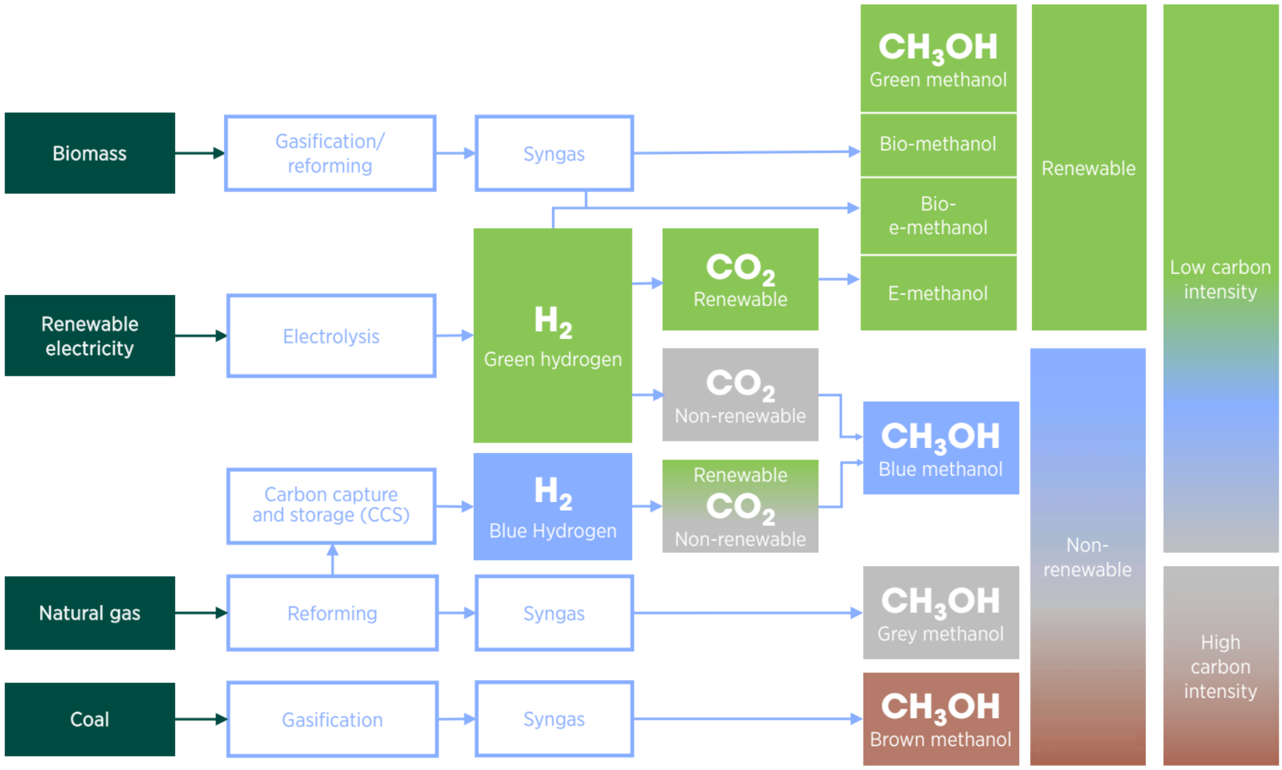

Figure 9: Main production routes of methanol; renewable CO_2: from bio-origin and through direct air capture (DAC), non-renewable CO_2: from fossil origin, industry; the suggested colour scheme for methanol is not standardised (source: IRENA and Methanol Institute, 2021)

In 2022, the global methanol demand can be accounted to 106 Mt. For fuel production, 11 % fall on gasoline blending, 7 % on methyl tertiary-butyl ether (MTBE), 3 % on biodiesel and 3 % on dimethyl ether (DME). As chemical intermediate, 31 % are led by methanol-to-olefins (for production of plastics, ethyl propylene, polypropylene), 23% by formaldehyde (for production of medium-density fibreboards, plywood), 7 % by acetic acid (for production of fleece, adhesives, paints), and 2 % each by methyl methacrylate (MMA), methylamines, methyl chloride (chloromethane) (MMSA, 2023a; Methanol Institute, 2023). Methanol can be further used as a fuel in direct oxidation methanol fuel cells (DMFC) to produce electricity – the current use is, however, limited to 0.02 % of the total demand (Azhari et al., 2022; MMSA, 2023).

E-methanol represents both an e-fuel and electrochemical. Beside e-methanol production via catalytic process while producing hydrogen from water electrolysis using renewable electricity, which represents mature technology (TRL 8-9), there are further two lab-scale approaches. The first one is based on the production of syngas parts CO and H_2 via electrolysis with the subsequent conversion of syngas to e-methanol, which needs, however, greater process efficiency. The second lab-scale approach encompasses electrochemical conversion of H_2O and CO_2, which also requires further efficiency gains. For the production of 1 tonne e-methanol based on water electrolysis with renewables, 0.19 t of H_2 (approx. 1.7 t H_2O), 1.38 t CO_2 and 10-11 MWh electricity (mainly for electrolyser with around 9-10 MWh) are needed (if CO_2 is externally supplied). The heat released during the process could be utilised for distillation of e-methanol. For the production of 1,000 t/d of e-methanol, an electrolyser with the capacity of minimum 420 MW_e would be required. In order to achieve the average daily production of 2,500 t e-methanol (s. above), an electrolyser with the gigawatt-capacity would be a prerequisite. The standard $CuO/ZnO/Al_2O_3$ catalyst would be required to be slightly adapted in order to handle the generation of greater amounts of H_2O during the e-methanol production process. These catalysts are already commodified and available at the market. The use of biogenic CO_2 for e-methanol production

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would result in net CO_2-neutrality. By 2050, the production of e-methanol is projected to be 250 Mt, which would need approx. 48 Mt of H_2 and 350 Mt of CO_2(IRENA and Methanol Institute, 2021) and is more than twofold of the total current primarily fossil-based methanol demand.

One further possibility could deliver the combination of biogas-based methanol production with electrolysis. In this case, CO_2 produced in the biogas process takes part in the reformer reaction alongside with CH_4, O_2 and steam. The alternative would be the addition of CO_2 from biogas to the process after the reaction in the reformer. For that, additional H_2 is needed for the optimum gas composition. Thereby, the reformer could be heated with RES electricity, which is under investigation. This type of process chain would result in greater carbon efficiency, since nearly all C contained in the raw material would be converted into C in methanol. The overall process efficiency of e-methanol production is 50-60 % (ibid.).

For the European Union, the aim is to substitute minimum 20 % of C used in the chemical and plastic products by sustainable non-fossil sourced C by 2030. In this respect, the production of methanol from CO_2 at reasonable costs would allow for production of a variety of chemicals such as propylene or ethylene which are used for the production of plastics, coolants, and resins (European Commission, 2021). The current production cost of methanol from natural gas in Europe can be amounted to ≥ 300 USD/t (IRENA and Methanol Institute, 2021). The current methanol contract price in Europe as of September 2023 is 386 USD/t, demonstrating easing prices since July 2023 (in comparison to 526 USD/t as of June 2023) (MMSA, 2023b). The current production cost for e-methanol is to be quantified at 820-1,620 USD/t. By 2050, the expected costs are 250-630 USD/t without carbon credits. The main influencing variables are the costs of H_2, which are coupled to the utilisation rate of electrolyser, costs of electrolyser and electricity, and CO_2. The partial integration of green e-methanol into the fossil production chain is seen as a transition possibility to stepwise master an economical production of e-methanol (IRENA and Methanol Institute, 2021).

3.2. Biopolymers, biochemicals and alternative sources of protein

The recovery and valorisation of CO_2 to produce high-value products holds immense significance and relevance in today's global context. In the face of critical challenges such as climate change and resource scarcity, leveraging CO_2 as a feedstock for manufacturing high-value recovered products emerges as a transformative solution. Among these, biopolymers, biochemicals, and protein sources stand out as marketable products experiencing significant global demand (Agnihotri et al., 2022; MarketsandMarkets, 2023; Witte et al., 2021). By utilising CO_2 as a building block for the synthesis of biochemicals and biopolymers, industries diversify their feedstock sources, thereby enhancing the supply chain sustainability, resilience, and security. Moreover, these value-added products find applications across a broad spectrum of sectors including pharmaceuticals, cosmetics, and feed and food additives, underscoring their versatility and potential impact on various industries.

Leading the way in this endeavour are bio-based non-biodegradable biopolymers, such as bio-based polyethylene and bio-based polyurethanes. Additionally, polylactic acid and polyhydroxyalkanoates (PHA) are anticipated to play a substantial role in driving growth within the domain of bio-based and biodegradable biopolymers (Aeschelmann & Carus, 2015). While biopolymers traditionally originated from first-generation sugars, ongoing research and development endeavours are exploring novel technologies that utilise agri-industrial waste, lignocellulosic materials, and gaseous feedstocks like biomethane or CO_2 as carbon sources. This shift towards alternative carbon sources aligns with the principles of a circular economy. Numerous pathways exist to convert CO_2 into value-added building blocks for biopolymer manufacturing. Microbial fermentation stands out as one such pathway where microorganisms utilise CO_2 as an input for biopolymer production. These microorganisms can produce and accumulate biopolymers like PHA and/or polyhydroxybutyrates (PHB) in their biomass, with applications in biodegradable plastics and other materials productions. This market is projected to reach USD 167 million by 2027, boasting a compound annual growth rate (CAGR) of 15.3 % (MarketsandMarkets, 2023). Within SEMPRE-BIO, PHA and PHB will be produced by employing a

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fermentation process culturing *Cupriavidus necator*, a chemolithoautotrophic bacterium that grows on mixtures of H_2 and CO_2 with no dependence on light availability. This bacterium naturally produces PHB using the CO_2 as a carbon source (Panich et al., 2021), showcasing a promising avenue for sustainable biopolymer production.

Regarding biochemical production resulting from CO_2 valorisation pathways, specialised microorganisms employed in fermentation processes can efficiently convert CO_2 into valuable biochemical compounds such as organic acids, amino acids, and bioactive molecules. These compounds find various applications in industries like pharmaceuticals, cosmetics, and food additives. The metabolic pathways involved in the production of organic acids (i.e., caproic acid and succinic acid) will be explored within SEMPRE-BIO. Both caproic acid and succinic acid have been chosen as they exhibit a growing market demand. The caproic acid market is projected to reach USD 52.8 million by 2027, growing at a CAGR of 5.6% over the analysis period 2020-2027. The global succinic acid market size was valued at USD 222.9 million in 2021 and is expected to expand at a CAGR of 9.7% from 2022 to 2030 (Agnihotri et al., 2022).

Caproic acid is an emerging platform chemical that can be produced from low-grade mixed organic waste. Recent demonstrations in both lab- and pilot-scale systems have shown high production rates and specificities under nonsterile conditions, highlighting its viability in continuous production (Chen et al., 2017). Caproic acid serves various industrial applications, functioning as a flavouring agent – especially in dairy products like cheese and butter – and as a plasticiser in rubber and plastics, including bioplastics. Additionally, caproic acid is used as a solvent in perfume and pharmaceutical manufacturing, as lubricant, and as a corrosion inhibitor in the oil and gas industry. Moreover, caproic acid can be used as an animal feed additive to enhance the growth and health of livestock (Berger, 2007; Conway, 1993; D`Mello, 2003). *Megasphaera elsdenii* demonstrates potential for caproic acid production, including the utilisation of CO_2 as a carbon source. The strain has been shown to produce caproic acid from various feedstocks (Kim et al., 2020). Additionally, studies have indicated that *M. elsdenii* is capable of fermenting different carbon sources to produce organic acids in the range of C2 to C6. Particularly for caproic acid, studies have reported the production of this acid by *M. elsdenii*, with concentrations of 0.88 g/L in specific culture conditions (Jeon et al., 2016).

Regarding succinic acid production, this organic acid stands as a valuable platform chemical with diverse industrial applications. Succinic acid serves as a crucial building block for biodegradable plastics such as polybutylene succinate (PBS) and polyethylene succinate (PES), which find utility in packaging, textiles, and agriculture mulching films. Moreover, succinic acid is integral in the synthesis of polyurethanes, contributing to the manufacturing of foams, adhesives, and coatings. Within the food and beverage industry, succinic acid is used as a flavoring agent and preservative in baked goods, dairy products, and beverages. Its applications extend to the cosmetics industry, where it serves as a pH regulator and moisturiser in products like skin creams, lotions, and hair care products. Within the pharmaceutical industry, succinic acid is used as an excipient in the manufacture of tablets and capsules (Bechthold et al., 2008; Mazière et al., 2017). The various CO_2 fixation processes have been optimised to achieve titers exceeding 100 g/L of succinic acid and productivities exceeding 3 g/L/h, rendering fermentative succinic acid production already cost-competitive compared to petrochemical-based strategies (Liebal et al., 2018). Within SEMPRE-BIO, the investigation focuses on cultures such as *Actinobacillus succinogenes*, a Gram-negative, capnophilic, facultatively anaerobic bacterium. This organism exhibits the ability to convert a broad range of carbon sources, including CO_2 HCO_3^-, and CO_3^{2-}, into succinic acid, showcasing an efficient and effective process (Xi et al., 2011). *Actinobacillus succinogenes* is employed for succinic acid production due to its native capacity to convert pentose and hexose sugars to succinic acid with high yield as a tricarboxylic acid cycle intermediate (Guarnieri et al., 2017). This bacterium is capnophilic, incorporating CO_2 into succinic acid, making it an ideal candidate for the conversion of lignocellulosic sugars and CO_2 to this acid. *A. succinogenes* is known for high yield production on various sugars in batch culture, and it has been shown to metabolise most naturally occurring sugars achieving volumetric productivities of 10 g/L/h (Brink & Nicol, 2014).

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SEMPRE-BIO will shed light over these promising valorisation alternatives for caproic and succinic acid production using recovered CO_2 and agri-industrial by-products, in particular digestate, as growing medium.

Concerning the global market for alternative proteins, a remarkable growth of up to 11% CAGR is anticipated within the 2020-2035 period, with microorganism-based sources reaching almost 23% of alternative protein human consumption (Witte et al., 2021). This shift is poised to significantly affect the livestock feed market, given that 57% of food system GHG emissions can be attributed to the production of animal-based food, comprising the protein supply (Xu et al., 2021).

The production of microbial protein, also referred to as single cell protein (SCP), has several advantages over other strategies such as plant-based protein and cultured meat. These advantages include the rapid growth of microbes, minimal land-use requirements, and high resource efficiency. A wide range of substrates, such as agri-industrial side-streams (e.g., simple carbohydrates and biomethane) and inorganic carbon from flue-gas streams (e.g., CO_2), hold potential as carbon and energy sources. One significant advantage of autotrophic routes lies in the direct fixation of CO_2 (Matassa et al., 2016; Ritala et al., 2017; Van Peteghem et al., 2022). The most matured dioxide-carbon-mitigate-SCP technology is microalgae cultivation, which shows a CO_2 fixation rate 10-50 times faster than land plants (Park et al., 2021; Wang et al., 2008). Moreover, it exhibits the potential to recycle CO_2 emissions from industry flue gases, with an average up-take of 1.8 kg CO_2/kg of dry weight biomass (Iglina et al., 2022; Rios & Luzzi, 2023). In addition, purple phototrophic bacteria (PPB) represent another group of microorganisms with SCP potential, capable of assimilating CO_2 by reducing it into organic feedstocks in the presence of organic matter as electron donor. This capability could eventually support cost-effective biogas upgrading (Marín et al., 2019). Both microalgae and PPB technologies show a crude protein content of around 60 % and possess a suitable amino acid profile, making them valuable for potential feed applications, alongside other commercial purposes including pharmaceuticals, cosmetics, biofuels, and biofertilisers (Hülsen et al., 2022; Saadaoui et al., 2021).

The global SCP market generated USD 5.3 billion in 2019, but it is expected to experience an annual growth rate of up to 5.5% by 2026 (360 Research Reports, 2021; Agnarsson et al., 2021). Furthermore, the global microalgae protein market is estimated to grow annually at a rate ranging between 6 and 7.8 % in the 2020-2027 term (Agnarsson et al., 2021). In 2021, 30 % of global microalgal production was sold to the feed industries (Lafarga et al., 2021). The average selling price of microalgae biomass stands at EUR 31/kg of dry weight (Rios & Luzzi, 2023), whereas, as feed additive, it can reach up to EUR 137/kg. High-value extracted products such as carotenoids, amino acids, PUFA (polyunsaturated fatty acids) extracts, astaxanthin, or erythrin multiply their market value, reaching up to 1,000 times their original worth (Rios & Luzzi, 2023; Saadaoui et al., 2021). Despite being presently considered a less competitive feed option due to high production costs, the situation may change soon with anticipated technical progress and diverse policy interventions related to imported feedstocks and carbon taxation.

The utilisation of waste streams, such as wastewaters and CO_2 emissions, as nutrient sources have a twofold positive impact on SCP production costs and environmental benefits. SEMPRE-BIO will focus on the production of alternative protein while valorising CO_2 recovered from biogas. Additionally, it will assess the microalgae and purple bacteria growth upon using nutrients derived from digestate. The CO_2 conversion into high-value protein biomass is affected by several key parameters, mainly related to strain selection and operational conditions during cultivation. Some of the most reported microalgae strains compatible with consumption in the EU, showing high proportion of crude protein, and exhibiting good CO_2 fixation rates (0.77-2.22 g/L/day) include *Chlorella vulgaris*, *Parachlorella kessleri*, *Tetradesmus obliquus* (Cheah et al., 2016; Onyeaka et al., 2021). Microalgae exhibit the ability to assimilate dissolved inorganic carbon in various forms. For example, *C. vulgaris* exclusively takes up gaseous CO_2, *S. obliquus* utilises both CO_2 and HCO_3^- through external carbonic anhydrase, and *C. kesslerii*, although lacking this enzyme, still utilises both CO_2 and HCO_3^- (Zhou et al., 2017).

The CO_2 assimilation, coupled with the optimal production conditions at the lowest possible cost, relies heavily on a well-designed photobioreactor (PBR) and carefully set operation conditions, especially at

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large scale. In the EU, closed PBRs dominate as the most common system for microalgae production at commercial scale (71 %), whereas open ponds and fermenters represent 19 and 10 % of the total production units, respectively (Araújo et al., 2021; Rampelotto & Hallmann, 2019). The closed PBR technology offers a variety of systems (e.g., panels, horizontal or vertical tubular, columns) and allows for stringent control of the environmental factors and biomass quality, thus simplifying applications for feed or food purposes. A PBR design based on a vertical tubular system coupled to a mixing-aeration tank enhances the photosynthetic efficiency and productivity of the production system (Acién et al., 2017; Narala et al., 2016). The previously mentioned microalgae strains, known for efficient CO_2 fixation, can yield up to 1.2 g/L/day when cultivated in such photobioreactors (Silkina et al., 2021; Zhou et al., 2017). SEMPRE-BIO will integrate all considerations and PBR design parameters to maximise biogenic CO_2 valorisation into high-value protein biomass.

In conclusion, the development of pathways to convert CO_2 into value-added biopolymers, biochemicals, and alternative sources of protein stands as a promising approach to address the challenges of climate change and resource depletion. The use of microbial biosystems for CO_2 valorisation has shown great potential in producing bio-based materials that can replace traditional petroleum-based products or effectively reintroduce biogenic CO_2 into the food/feed chain. The growing market demand for these goods highlights the importance of developing sustainable pathways for CO_2 utilisation.

3.3. Overview and mapping of biogas and biomethane plants with CO_2 valorisation in Europe

The following depictions are based on the results of literature research and conducted surveys as described above in sections 2.1 and 2.2. They do not claim to be complete, but rather provide an insight into the currently changing market of biogenic CO_2 valorisation on the basis of the determined data sample. Thereby, the focus is clearly on commercial-scale CCU facilities without detailed elaboration of lab- and demo-scale projects or consideration of possible CCS developments. In the following, the literature sources are summarised and denoted as DBFZ literature review, 2023. A precise attribution of the literature sources differentiated by the status of the biogas and biomethane plants with CO2 valorisation in Europe (in operation vs. in the planning stage) can be found in Table 4 in Annex.

Valorisation of biogenic CO_2 derived from biomethane plants represents a dynamic and steadily growing segment in Europe. The Netherlands and the United Kingdom can be seen as the pioneers in CO_2 valorisation from biogas upgrading with CO_2 utilised primarily for air enrichment in greenhouses in order to speed up the photosynthesis rate and to increase the yields. One of the first CO_2 capture units for the use of CO_2 in greenhouses was commissioned by Eco Fuels in 2011 in Well, the Netherlands (EcoFuels, 2023; Pentair, 2023). Relevant for the opening up the market towards further valorisation sectors in Europe, especially food and beverage industry, was the launch of the document 70/17 Carbon Dioxide Food and Beverages Grade, Source Qualification, Quality Standards and Verification by EIGA in 2017, as described above in section 3.1.3 in Excursus 3. According to that, CO_2 from AD based on energy crops was on par with CO_2 from yeast-based fermentation (ethanol production), whereas CO_2 from co-digestion or organic waste requires additional care in evaluation (EIGA, 2017).

The second wave in terms of timing was taken over by Denmark and Italy, however, with different type of development. Whereas Denmark set on very large capture capacities of biogenic food-grade CO_2 with its flagship project in Korskro with the annual capacity of 16,250 t/a, which are able to cover 25 % of its national CO_2 demand (IEA Bioenergy Task 37, 2020; DBFZ survey of 4 Horizon Europe projects on biomethane, 2023), Italy introduced mainly middle to large-scale capacities of around 7,200 t/a of biogenic CO_2. Now, new markets emerge in France and Germany, whereby due to the smaller biogas upgrading capacities in France in comparison to Germany French CO_2 capture units both in operation and under construction tend to have capacities in the smaller range of around 3,200 t/ a of biogenic CO_2 (with the exception of a few examples) (DBFZ literature review, 2023; DBFZ survey of 4 Horizon Europe projects on biomethane, 2023; DBFZ survey of the German biomethane plant operators, 2023).

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An overview of the biogas and biomethane plant sites with CO_2 valorisation both in operation (current and expected by the end of 2023) and in the planning stage in Europe can be found in Figure 10. In accordance with that, as of 10/2023 Italy, the Netherlands, and the United Kingdom (including Scotland and Northern Ireland) are leading the way in biogenic CO_2 valorisation from commercial-scale biogas and biomethane facilities in Europe (60 % in total), followed by Germany and France (the latter especially due to the recent development in 2022/2023). For the years to come, the high number of biomethane plants with planned CO_2 valorisation especially in Germany is based on the results of the literature research, DBFZ survey of 4 Horizon Europe projects on biomethane, 2023 and DBFZ survey of the German biomethane plant operators, 2023. The latter represents the national empirical data collection without having respective national counterparts in other studied countries. From 32 German biomethane plant operators participated in the national empirical data collection, 10 have stated to plan to capture and valorise their biogenic CO_2 in 2024, 2025 and 2027 (DBFZ survey of the German biomethane plant operators, 2023).

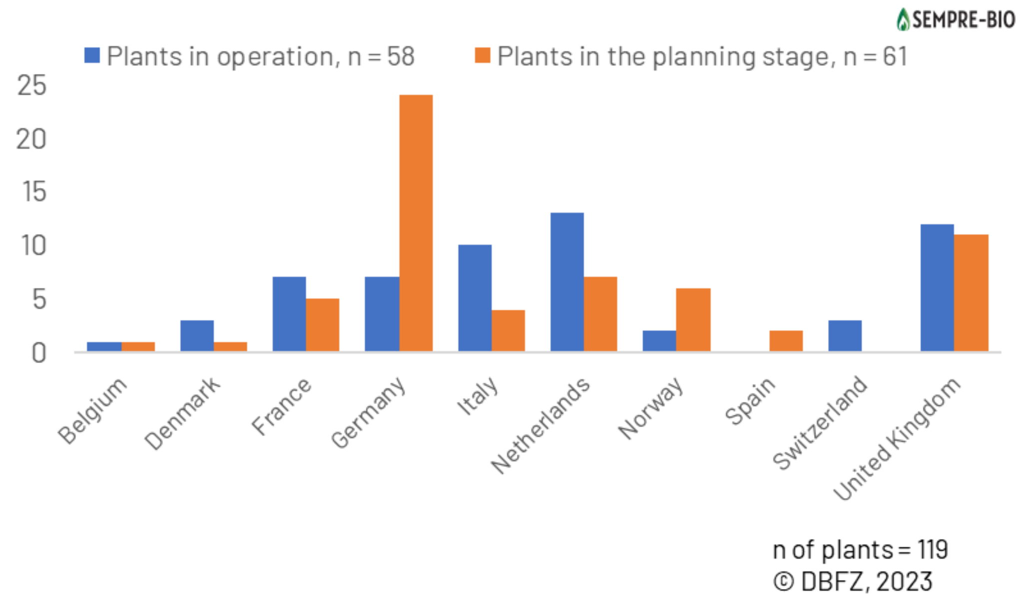

Figure 10: Biogas and biomethane plants with CO_2 valorisation (commercial-scale CCU) in Europe as of 10/2023, the planning stage refers to the installation of CO_2 capture units; United Kingdom including Scotland and Northern Ireland (source: based on DBFZ literature review, 2023; DBFZ survey of 4 Horizon Europe projects on biomethane, 2023; DBFZ survey of the German biomethane plant operators, 2023)

The planning horizon of the announced projects (planning stage) ranges from the end of 2023 (25 %) for the years to come 2024-2025 (73 %) up to 2027 (one unit) (DBFZ literature review, 2023; DBFZ survey of 4 Horizon Europe projects on biomethane, 2023; DBFZ survey of the German biomethane plant operators, 2023). The intended commissioning can depend, however, also on possible non-economic barriers. As described below in subsection 3.4.2 in case of Acorn Bioenergy Limited approaching different sites in the UK and Scotland, there are residents' protest movements especially against erection of the new AD facilities or the planning application submitted by the company being rejected by the planning authorities partly as a result of local public debate (The Press and Journal, 2023b). Public acceptance is not a new or regionally limited aspect and can be both a driver and an impediment issue for development of biogas and biomethane production, even when coupled with biogenic CO_2 capture.

The distribution of the specific types of uses for biogenic CO_2 for capturing sites in operation (current and by the end of 2023) and in the planning stage can be found in Figure 11. Thereby, multiple uses of biogenic CO_2 per plant (also referred to as mentions) are possible. Certain types of uses such as dry ice production, CO_2 blasting or cooling agent are shown separately, since there is no further indication of the specific final industry. In operating biomethane plants, the focus is clearly on CO_2 valorisation in greenhouses with 35 % and food and beverage industry with 27 %. For the latter, biogenic CO_2 amounts

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are utilised in 13 % of mentions specifically for the production of carbonated beverages. To a smaller extent, the captured CO_2 is used for PtX technologies (10 %), dry ice (8 %) or as a cooling agent (8 %). Further utilisation sectors such as chemical industry, healthcare sector or pharmaceutics play a minor role. This might be due to the fact of sensitivity of the topic that the specific final industrial uses are probably not mentioned in publicly available sources. Further, if there are no direct sales of the produced CO_2 to the final customers and sales contracts are concluded with the large suppliers of industrial gases such as Air Liquide S.A., the Linde Group, the Messer Group GmbH, Nippon Gases or others, the actual final uses and the respective exact amounts might remain unknown or are traceable with additional effort (based on an accounting system with the bills of delivery stating exact quantities and target customers from the side of the industrial gas traders).

In comparison to the current utilisation pathways, the situation for the announced facilities changes towards relative increase of CO_2 use in the food and beverage sector with 47 % (almost a half of that dedicated specifically to carbonated beverages) as well as the increment of PtX technologies to 22 %. In contrast, the utilisation of CO_2 in greenhouses moves somewhat into the background (13 %). A change towards the production of high-value biogenic CO_2-based products is not yet apparent, according to the announced and available targets. In addition to sensitivity issues, the missing information may also be due to the fact that the collected sample data primarily includes commercial-scale facilities, whereas lab- or demo-scale projects were not initially mapped within the scope of this report.

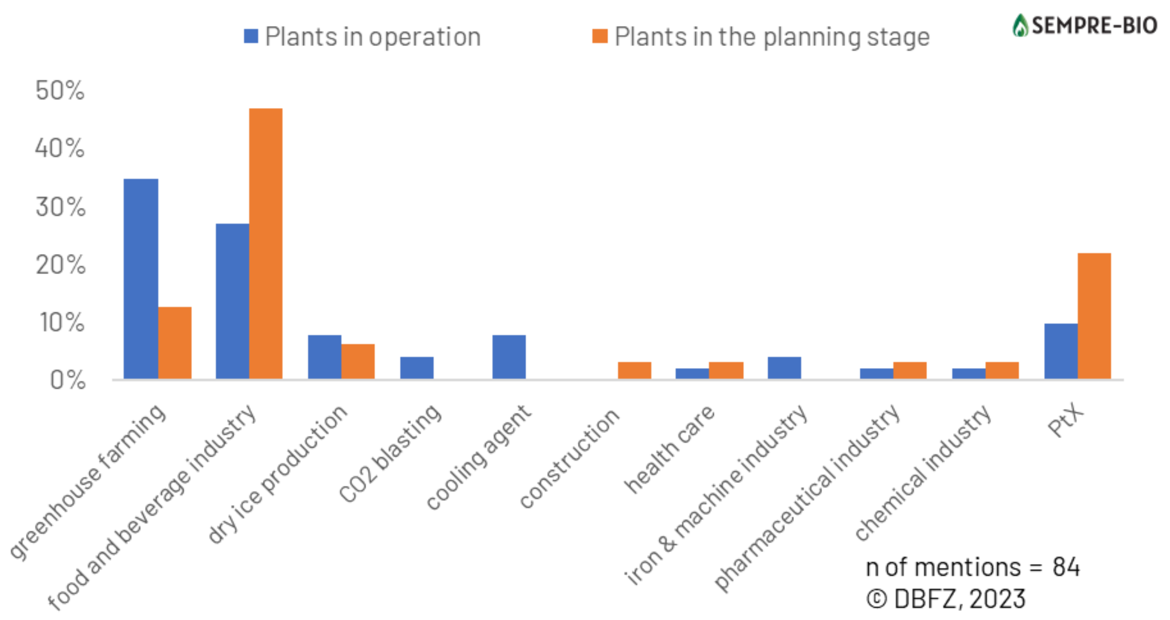

Figure 11: Distribution rate of different types of CO_2 valorisation at operational (current and by the end of 2023) and announced CO_2 capture sites at biogas and biomethane plants in Europe (operational and announced commercial-scale CCU), as of 10/2023; number of mentions (source: based on DBFZ literature review, 2023; DBFZ survey of 4 Horizon Europe projects on biomethane, 2023; DBFZ survey of the German biomethane plant operators, 2023)

Where available, the type of very precise information on final sector use or direct sales of biogenic CO_2 to customers are described in the project examples below in chapter 3.4. For instance, Apsley Farms in the Bourne Valley in the UK operates direct sales of its biogenic CO_2 using their in-house lorry fleet of CO_2 tankers supplying CO_2 for different industry sectors such as automotive, food and beverage, metal fabrication, water treatment, oil & gas, and dry ice (Apsley Farms, 2023). In Denmark, biogenic CO_2 from the Korskro showcase project is traded under the own trade mark GO' CO_2 (IEA Bioenergy Task 37, 2020). By buying the locally produced CO_2 at the biomethane plant in MéthaTreil, France for their greenhouses, a local vegetable grower Vinet Frères group secures a fixed, non-seasonal price for CO_2 covering 35 % of their annual CO_2 demand (Association d'Initiatives Locales pour l'Energie et l'Environnement, 2021). The proximity to customers, local and biogenic origin, green label, high purity grades and almost complete absence of impurities, safeguarded projected supply amounts and the possibility of the fixed

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non-seasonal price are obviously competitive advantage of biogenic CO_2 from biogas and biomethane in comparison to its fossil-derived counterpart.

With respect to the emerging CO_2 valorisation at bio-LNG plants in Europe as described in Excursus 1, from the currently 15 bio-LNG plants in operation 11 with CO_2 valorisation could be identified with 5 of them being located in Italy. Regarding the future projection, 17 bio-LNG facilities with CO_2 capture units could be identified with 5 each being announced in Germany and Norway. For development in Germany, this corresponds with the envisaged expansion target capacity of 4,324 GWh/a of bio-LNG by 2025. For Norway, this is especially true due to the fact of its first mover status starting bio-LNG production already in 2012 as well as 97 % of the in 2021 produced biomethane being used in transport sector (European Biogas Association, 2022b). Regarding further bio-LNG production sites in Europe both commissioned and under development, there is no additional, easily accessible information on the CO_2 valorisation coupled to bio-LNG production.

Mapping of the biogas and biomethane plant sites with CO_2 valorisation (current and expected by the end of 2023) in Europe can be found in Figure 12 below, whereas an interactive mapping of facilities will be available on the website of SEMPRE-BIO (https://sempre-bio.com/) and will be part of WP 6 Connect, communicate, exploit, replicate based on the data provided by DBFZ. It is evident that the majority of sites (60 %) with CO_2 valorisation (current and expected by the end of 2023) are concentrated in the Netherlands, the south of the United Kingdom, and the north of Italy, followed by north-western Germany and France (23 %). With respect to the capacities, for almost 50 % of the plants no annual capacity data are provided. For the remaining 50 %, the capacity ranges are distributed evenly except the expected highest annual CO_2 production capacity > 20,000 t/a located in Friesoythe, Germany. Regarding the current valorisation sectors of CO_2 from biogas and biomethane, almost a quarter is attributable to the greenhouse farming, followed by food and beverage industry (12 %), industrial gas applications (12 %) as the only sector or both in combination (12 %), while energy generation accounts for 10 %. In addition, 72 % of the CO_2 capture sites being currently in operation produce CO_2 from biogas and biomethane in food-grade quality according to the specification of EIGA or ISBT. Thereby, the food-grade CO_2 has been valorised not only in the food and beverage sector but also for other applications. A detailed overview of the illustrated sites can be found in Table 5 in Annex.

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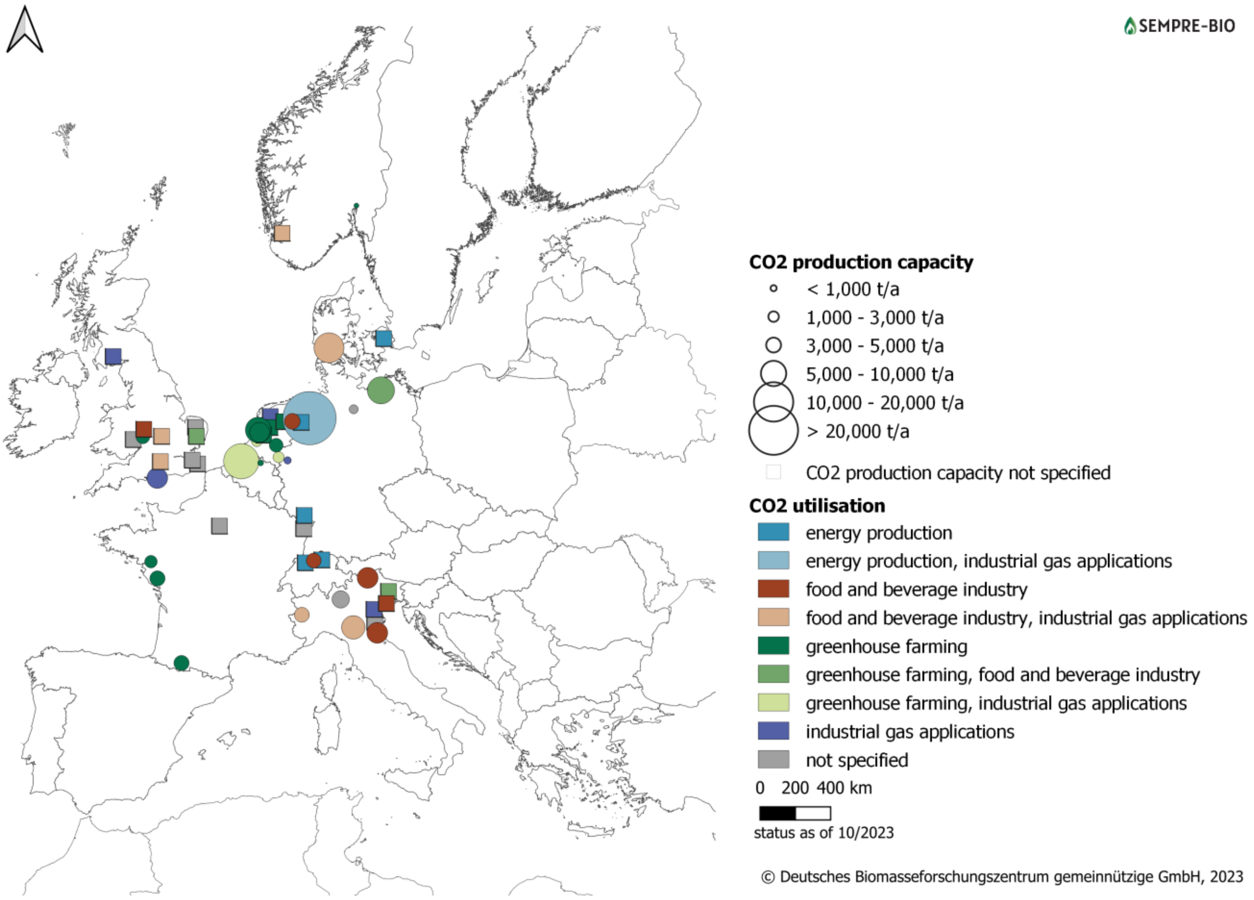

Figure 12: Map of biogas and biomethane plant sites with CO_2 valorisation (current and expected by the end of 2023) in Europe (commercial-scale CCU), differentiated by CO_2 production capacities in tonnes per year and type of CO_2 utilisation as of 10/2023 (source: based on DBFZ literature review, 2023; DBFZ survey of 4 Horizon Europe projects on biomethane, 2023; DBFZ survey of the German biomethane plant operators, 2023)

3.4. Project examples of biogenic CO_2 valorisation from biogas and biomethane

In the following, the selected project examples of biomethane sites with CO_2 valorisation in Europe are described differentiated by country, type of CO_2 use, status, production size, and type of input materials. The project examples were selected based on their pioneering character in the respective countries in terms of the range of different CO_2 valorisation options, the size of CO_2 capture capacities, first mover and/or innovative character, specific features such as direct sales of the biogenic CO_2 using the own in-house lorry fleet of CO_2 tankers or own trade-mark for distribution of biogenic CO_2 and completeness of the available information on the parameters mentioned above.

3.4.1. The Netherlands

EcoFuels, Well

The biomethane plant in Well (municipality Bergen in the province Limburg, southeast of the Netherlands) went into operation in 2011 based on the biogas plant built in 2006 with the total capital expenditure of EUR 13 mill. The plant is operated by EcoFuels originated by the Dutch company, a vegetable grower, processor and vendor Laarakker Groenteverwerking B.V. (growing 110,000 t/a of vegetables on 3,500 ha) and an industrial and household waste management company Indaver Nederland B.V. As substrate 120,000 t vegetable and organic (such as foodstuffs with expired expiry date) waste are used which are supplied partly by the Laarakker Groenteverwerking and partly by ISO- or HACCP-certified external suppliers from agriculture, horticulture, and the processing and food industry.

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For biomethane and liquid CO_2 production, Pentair Haffmans' membrane and cryogenic technology is used. The upgrading capacity of the plant is 340-365 m^3_{STP}/h with the annual biomethane production of 2,800,000 m^3_{STP} (enough to supply 1,900 households with gas) and liquid CO_2 production of 2,000 t/a. Besides, 17,000 MWh_e of electricity (with a minor part for self-consumption and the remaining share enough to supply 5,800 households or the whole municipality Bergen, where the plant is located) and 16,000 MWh_{th} of heat used for the fermentation process as well as for drying processes, and fertiliser or digestate-based extraction of nitrogen and phosphate are generated on an annual basis. The produced biomethane is injected into the gas grid in accordance with the Dutch requirements, whereas food-grade CO_2 is used for fertilisation in greenhouses, as CO_2 blasting in the purification industry and for dry ice production for cooling the food and for refrigerated transport of vaccines. Depending on the market developments, the production of bio-LNG can take place in the future (EcoFuels, 2023; Pentair, 2023).

SFP Zeeland B.V., Westdorpe

The biomethane plant located in Westdorpe (municipality Terneuzen in the province Zeeland, southwest of the Netherlands) went into operation in 2019. It was taken over in 2021 by SFP Zeeland B.V. The system uptime was maximised in order for the downtime to be amounted to 1 day/a. There are 9 digester tanks on site with the fermenter volume of 10,000 m^3 each. The applied technology is a combination of membrane and the cryogenic unit from Pentair Haffmans. The upgrading capacity accounts for 5,000 m^3_{STP}/h biomethane. The current biomethane generation is 40,000,000 m^3_{STP}/a (enough to supply 25,000 households) with biomethane being injected into the national gas grid. The digestate production is 150,000 t/a with the separation of the liquid and solid fractions and the latter being composted in composting tunnels. The liquid CO_2 production accounts for 20,000 t/a and EIGA/ISBT-grade CO_2 is used as fertiliser in greenhouse farming treating the total surface area of 400 ha (Pentair, 2022a; Sustainable Fuel Plant, 2023a; European Biogas Association, 2023).

3.4.2. The United Kingdom

Springhill Farms, Pershore, Worcestershire

The biomethane plant at the Springhill Farms in Pershore (ceremonial county Worcestershire) commissioned in 2013 operated by Vale Green Energy was the first plant with biomethane upgrading and injection into the national gas grid and parallel CO_2 recovery in the United Kingdom. The decision to erect a new AD facility with subsequent biomethane upgrading was motivated by the new legislation forbidding the return of untreated vegetable-based residues from 809 ha farmland and 12 ha greenhouses as fertiliser to the agricultural land. There are 2 digester tanks on site with the fermenter volume of 4,200 m^3 in total. As substrate, 70 t/d of grass, maize, sugar beet and wheat are used. The technology is based on the combined membrane and the cryogenic unit from Pentair Haffmans. The annual biomethane generation can be amounted to 1,630,000 m^3 biomethane (enough to supply 1,000 households), whereby 25 % of the produced gas are used for the own power and heating demand with the recovery of 3,000 t/a of CO_2. The produced biogenic CO_2 is used according to the pre-defined dosing and timetable for fertilisation in tomato greenhouses of the farm leading to 15 % of the tomato yield increase (Pentair, 2020; den Heijer and Coenradie, 2017; Gasworld, 2014; Vale Green Energy, 2023).

Apsley Farms

Commissioned in 2014, the biomethane plant at Apsley Farms in the Bourne Valley (Andover, southern English county of Hampshire) is now the third largest producer of biomethane in the United Kingdom. The farm total area accounts for 425 ha with 364 ha being arable land. The substrate for AD, mainly maize and rye silage, is delivered by 40 farms from the region. The daily biomethane production accounts for 28,800 m^3. There are 2 CHP units on site with the total installed electrical capacity of 1.1 MW used for electricity production in order to cover own demand for plant operation as well as for domestic and

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commercial properties of the farm while the rest is supplied to the electricity grid. The digestate and garden mulch produced are certified by the Soil Association for the use on organic soils.

The CO_2 liquefaction unit was added in 2016. The daily production of biogenic CO_2 can be amounted to 32 t. Apsley Farms provide direct sales of food-grade biogenic CO_2 (with the purity of 99.99% and storage capacities of 150 t CO_2 on site) as bulk orders between 1 and 20 t using their in-house lorry fleet of CO_2 tankers supplying CO_2 for different industry sectors such as automotive, food and beverage, metal fabrication, water treatment, oil & gas, and dry ice. The farm invested into the CO_2 testing laboratory enabling CO_2 testing services onsite (Apsley Farms, 2023; den Heijer and Coenradie, 2017; Sustainable Bourne Valley, 2023).

Crofthead Farm, Scotland

For the production of dry ice, the CO_2 capturing, purification and liquefaction unit was established in 2022 on behalf of Dry Ice Scotland Ltd at the AD plant of the Crofthead Farm (located in Crocketford, in the Dumfries and Galloway council area near the boundary between Scotland and England). The substrate amount for biomethane production accounts for 100,750 t/a consisting of manure, poultry litter, cattle slurry, energy crops, whey and distillery by-product liquid feeds. The liquid CO_2 will have the food-grade quality and can be stored in two storage tanks (62,000 kg) on site. The production of dry ice occurs when the liquid CO_2 is brought to atmospheric pressure resulting in "snow" being pelletised and passed to a slicing machine. The solid dry ice is then stored in specialised palletised packaging for 3 to 7 days with the total production of dry ice expected to be 8,000 t/a. It can be used as a vaccine or for biological sample transportation, cold-chain logistics, and transporting perishables for both short and long-distances. The investment volume for the CO_2 recovery and dry ice production facility can be amounted to £4 million with about £3 million being grant funding. The technology provider is Pentair Haffmans B.V. (Carbon Capture Scotland Limited, 2022; Pentair, 2022b; The Herald, 2021).

Acorn Bioenergy Limited

Since 2022 Acorn Bioenergy has been approaching different sites in Scotland and the United Kingdom in order to build AD plants with CO_2 recovery on site. The aimed substrates for biomethane production are silage (rye, maize and grass), straw, poultry litter, farmyard manures in combination with draff, pot ale, pot ale syrup – in case of the future plant sites near Scottish distilleries – with the total substrate amount around 90,000 t/a. The sites are located in Evenley (targeted biomethane production of 9,000,000 m^3), Winchester (targeted biomethane production of 9,753,325 m^3), Wherwell, Tysoe (UK) and Balintore, Elgin, and Rathven (Scotland) with intended commissioning in 2024 and 2025. Not all of the AD facilities will be able to inject the upgraded biomethane on site since they won't be connected to the gas grid directly. In some cases, there are residents' protest movements especially against erection of the new AD facilities resp. the planning application submitted by Acorn Bioenergy being rejected by the planning authorities, partly as a result of local public debate. The planned CO_2 production capacity moves within the same range for all locations and amounts to approx. 13,000 t/a. The future CO_2 valorisation sectors are agriculture, food and beverage industry, construction and health care, and in some cases hydrogen technologies, and sustainable aviation market (Acorn Bioenergy, 2022a; Acorn Bioenergy, 2022b; Acorn Bioenergy, 2023a; Acorn Bioenergy, 2023b; Acorn Bioenergy, 2023c; Andover Advertiser, 2022; Bioenergy Insight, 2022b; Evenley Parish Council, 2022; The Press and Journal, 2023b; Tysoe Parish Council, 2022b; Winchester Action on Climate Change, 2022).

3.4.3. Denmark

Nature Energy Korskro A/S

The biomethane plant in Korskro (located on the west coast of the Jutland peninsula in southwest Denmark) was commissioned in 2019 being the first biomethane plant with CO_2 recovery in Denmark and

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one of the largest biomethane plants in the world. The substrate for AD is provided by 603,500 t/a of manure from cattle, pigs, and minks, and 106,500 t/a from animal bedding, food waste, industrial and retail residues, and to a minor share by energy crops. The annual biomethane generation can be amounted to 49,000,000 m^3 biomethane, whereas the ISBT-grade CO_2 production accounts for 16,250 t/a with further capacities to purify and liquify additional CO_2 amounts. The CO_2 is traded under the own trademark GO' CO_2 covering one quarter of the total annual Denmark's CO_2 consumption. The CO_2 utilisation sectors are food and beverage, iron & machine, healthcare, and pharmaceutical. The biomethane plant in Korskro is operated by Nature Energy Biogas A/S, which is the largest biogas producer in Denmark. Nature Energy was acquired by Shell Petroleum NV in September 2023 (IEA Bioenergy Task 37, 2020; DBFZ survey of 4 Horizon Europe projects on biomethane, 2023; Nature Energy, 2023).

3.4.4. Norway

Den Magiske Fabrikken AS

The extension to the upgrading capacity 2,400 m^3_{STP}/h of biogas to biomethane for Den Magiske Fabrikken AS (The Magic Factory) site located in Sem (village in Tønsberg, Vestfold county, eastern Norway) was announced in spring 2023 representing the third plant extension (Malmberg, 2023). Den Magiske Fabrikken AS is the common plant of the region Grenland and Vestfold. The substrate treatment capacity as of 2022 comprises around 165,000 t/a of food waste, livestock manure, and industrial waste. The produced biomethane is sold to Air Liquide Skagerak which supplies biomethane mainly to public transport. A part of the biogenic CO_2 flow from biomethane production is captured and utilised by the nearby industrial, semi-closed pilot with the initial amount of approx. 400 t/a for tomato production (Malmberg, 2023; Østfoldforskning, 2020; Hydrogen24, 2022; Reklima, 2023).

Renevo AS

Renevo AS is a company that will produce liquefied biomethane for the transport market (LNG), biofertiliser and biogenic CO_2. In the autumn 2020, Shell's gas distributor Gasnor acquired 50 % of the shares in Renevo, formerly known as Sunnhordland Naturgass. In 2022, the biomethane plant in Stord municipality (western Norway) was re-opened by Renevo AS after the expansion of the capacity and substrate input to 55,000 t/a (42,500 t/a cattle manure, 11,250 t/a salmon farming waste, 1,250 t/a fish sludge). The plant is expected to produce 8 t/d of bio-LNG and 10 t/d of biogenic CO_2. Renevo AS signed an agreement with Nippon Gases Norway AS, the largest supplier of CO_2 for commercial use in Norway, on biogenic CO_2 from the plant site in Stord municipality to be used for cooling, water treatment, production of dry ice and carbonated beverages (Cryo Pur, 2023; Renevo, 2022b; Nippon Gases, 2022; iLaks, 2021). The second plant of Renevo AS now being built in Etne municipality (Vestland county, western Norway) will be almost twice the size of the plant at Stord with the total substrate input of 110,000 t/a (manure, fish waste, slaughterhouse and food waste) producing bio-LNG and liquid CO_2 for industrial uses. The planned commissioning date is in 2024. The total investments into Etne site can be amounted to NOK 200 million, with NOK 60 million in Enova SF (state enterprise owned by the Norwegian Ministry of Climate and Environment) funding. The technology provider for purification and liquefaction of biomethane and production of liquid CO_2 for both sites in Stord and Etne is the French company Cryo Pur (iLaks, 2021; Renevo, 2022a; Renevo, 2023; NTB Kommunikasjon, 2022). Renevo AS plans to build further 10 biogas plants in Norway and considers industrial sites in Jondal, Kvinnherad, Mongstad, Hadsel, Tromsø, Rogaland, and Vestland north (Renevo, 2022a).

3.4.5. Italy

Biogas Wipptal

Located in South Tyrol, Biogas Wipptal, the enterprise consisting of 60 dairy farmers from the Valle Isarco region, has been producing liquid food-grade CO_2 since 2022 in the amount of 7,000 t/a. Biogas

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Wipptal supplies the produced biogenic CO_2 to the food and beverage industry in the region which used to purchase fossil CO_2 from ammonia production or to import fossil CO_2 from Hungary. The CO_2 demand of the beverage industry in the regions South Tyrol, Vorarlberg and Tyrol accounts for 27,000 t/a. In this way, CO_2 produced by Biogas Wipptal could cover 25 % of the local CO_2 demand for beverages. For biomethane production the plant utilises 150,000 t/a of substrate input consisting of 40 % of bovine waste and 60 % of bovine liquid manure provided by 130 farmers from the region. In addition, 4,000 t/a of bio-LNG are produced. The total investment into the CO_2 liquefaction unit and bio-LNG production can be amounted to 20 million EUR (Biogas Wipptal, 2023; CNG Mobilty, 2023; Biogas Wipptal, 2021).

Caviro S.p.A. (Faenza, province Ravenna)

Caviro is an agricultural cooperative consisting of 29 members, 27 of which are social wine cellars, around 11,650 winegrowers located in 7 regions of Italy (Veneto, Emilia-Romagna, Tuscany, Marche, Abruzzo Apulia and Sicily). The AD plant was commissioned in 2019 representing the largest of its kind in Italy with the annual biomethane production capacity of 12,000,000 m^3_{STP}. The substrates for biomethane production are provided by the waste from the processing of winemaking by-products and wastewater with a total amount of 385,000 t/a. In 2020 the CO_2 recovery and purification plant, derived from the methane production process, came into operation. The plant is able to produce 7,000 t/a of liquefied CO_2 with the purity grade of 99.95 % (food-grade) supplied mainly to carbonated beverage sector. In addition, at the Faenza plant site, there is also bioethanol production. Further, there is a company subsidiary Enomondo which is owner of the biomass cogeneration plant supplying the Faenza site with the renewable energy. Further 170,000 t of waste, consisting of marc and pomace are delivered to Enomondo in order to produce a portion of the biogas resulting from the AD process which is converted into electricity (84,000 MWh_e) and thermal energy (114,000 MWh_{th}). In 2021 it was announced that Caviro is going to build one of the largest bio-LNG plants in Europe with an annual capacity of 9,000 t (Caviro Extra, 2023, Enomondo, 2023; HAM, 2021; DBFZ survey of 4 Horizon Europe projects on biomethane, 2023).

3.4.6. France

The French company branch Verdemobil BIOCO_2 produces biogenic CO_2 using cryogenic distillation. After membrane purification of the biogas, the CH_4 is injected into the network, while the lean gas is cleaned again to obtain almost 100% CO_2 using a cold distillation process called Carboliq. The carbon dioxide is then compressed to 20 bar before being cooled to -20 °C to allow it to liquefy. The technology was developed by the start-up CryoCollect. With all its modules installed by the end of 2023 in France, the company will recover around 35,000 t of CO_2 per year. The company will strengthen its pricing power and indicates that there are potentially 118 directly eligible sites in France for CO_2 capture and liquefaction. There are contracts signed for 8 additional sites for the installation of CO_2 liquefaction units and for 27 sites, there are negotiations in progress (Verdemobil Biogaz, 2023a; Verdemobil Biogaz, 2023b).

The biomethane plant in MéthaTreil (municipality Machecoul-Saint-Même, department of Loire-Atlantique, western France) was commissioned in 2017 based on the previous cogeneration project. CO_2 liquefaction from Verdemobil with the capacity of 2,500 t/a has been operational since September 2020. The SAS has invested €1 million to recover its CO_2 and expects a return on investment after 9 years. It received a 30% subsidy to finance this project. The substrates used for biomethane generation are 2,800 t/a of cattle slurry, 5,880 t/a of straw manure, 5,480 t/a of intermediate energy crops, 2,000 t/a of maize and 1,500 t/a of market garden waste (tomatoes, lettuce, potatoes, etc.). The CO_2 is stored in a 60 m^3 vertical tank, before being transported once or twice a week by a 20 m^3 tanker. By buying the locally produced CO_2 for their greenhouses, a local vegetable grower Vinet Frères group secures a fixed, non-seasonal price for CO_2 covering 35 % of their annual CO_2 demand (Verdemobil Biogaz, 2023a; Association d'Initiatives Locales pour l'Energie et l'Environnement, 2021).

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3.4.7. Switzerland

Recycling Energie AG

Recycling Energie AG in Nesselnbach is the largest biomethane plant in Switzerland. From around 20 % of the food waste generated in Switzerland, biomethane but also heat and electricity are produced on site. The CO_2 liquefaction unit was supplied by the Swiss company Hitachi Zosen Inova and commissioned in July 2023 and the costs for the project can be amounted to CHF 3 million. The annual CO_2 production accounts for 3,500 t with biogenic CO_2 being utilised in the food and beverage industry. Pivotal for the project development was the creation of the business case in order to define future customers for CO_2 but also the initiation of the proof for CO_2 compensation which allows for an acceptance of the compensation certificates for a fixed term at a fixed price. Relevant was also the analysis of the demanded quality of the liquid biogenic CO_2. In case of Recycling Energie AG the future customer was initially one Swiss industrial gas trader which would otherwise supply the imported fossil CO_2 (Swisspower, 2022; Hitachi Zosen Inova, 2023; ArgoviaToday, 2023; energie bewegt winterthur, 2023).

Limeco, Dietikon

The first industrial Power-to-Gas plant in Switzerland is operated by the Swiss energy supplier Limeco and was commissioned in April 2022 with the total investment costs of CHF 14 million which were co-invested by 8 Swiss energy suppliers providing the generated renewable gas to their end consumers. The project was also funded by the cantonal Office for Waste, Water, Energy and Air AWEL. Electrolysis with the capacity of 2.5 MW splits water into gaseous hydrogen and oxygen with the aid of electrical energy. In order to produce 450 m^3 hydrogen per hour, 10,000 till 15,000 MWh/a of renewable electricity provided by the waste-to-energy plant are used. The hydrogen is mixed with CO_2 from 1,800,000 m^3/a of sewage gas provided by the nearby wastewater treatment plant which leads via the biological methanation to the production of CH_4 and water. The generated gas is then upgraded and injected into the gas grid supplying an equivalent amount of energy of 18,000 MWh/a. In this way, a CO_2 reduction of 4,000 to 5,000 t per year can be achieved. The electrolysis was supplied by Siemens Energy AG, whereas the methanation reactor was provided by the German Hitachi Zosen Inova Schmack GmbH (HZI Schmack), a subsidiary of the Swiss Hitachi Zosen Inova AG. However, due to the energy deficiency in the winter 2022/23, the PtG plant was shut down with the reason that it is not justifiable to produce biogas from the scarce electricity, since the conversion losses are not negligible. Therefore, all electricity produced by the waste-to-energy plant was fed completely into the electricity grid instead of being partially used for electrolysis (Limeco, 2022; Limeco, 2023).

3.4.8. Germany

Bioenergie Güstrow GmbH

At the site of the Bioenergie Güstrow GmbH located in Güstrow (federal state Mecklenburg-Vorpommern in north-eastern Germany) one of the biggest German bio-LNG plants with CO_2 liquefaction was taken into trial operation at the end of August 2023. Previously, the site run the biomethane production on 400,000 t/a of substrates including maize, whole crop silage, cereals and grass silage. In the course of remodelling work, the substrate input was reduced to around 150,000 t/a consisting of 100,000 t/a of chicken manure and 40,000 t/a of energy crops and additional CHPs for own power supply were adjusted to 3.1 MW_e. It is expected that the site will provide 9,600 t bio-LNG per year in parallel to 15,000 t/a of liquid food-grade CO_2 which can be used in the food industry or greenhouse farming. There is a 300,000-litre tank for liquid CO_2 on site. The total investment costs in a CO_2 liquefaction unit, an LNG plant for the liquefaction of biomethane and replacement investments can be amounted to over € 50 million. The plant owner is the German EnviTec Biogas AG which plans the commissioning of further bio-LNG sites with parallel CO_2 liquefaction in Germany (Forst, Neuburg/Steinhausen, and Suckow/Sachsendorf with

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the total expected investment volume of € 47.5 million for all three sites) (EnviTec Biogas, 2023a; EnviTec Biogas, 2023b; EnviTec Biogas, 2022).

Nordfuel Friesoythe

One of the biggest bio-LNG plants in Europe is now built by the German plant constructor revis bioenergy GmbH at the c-Port on the Coastal Canal in Friesoythe (district of Cloppenburg, federal state Lower Saxony, north-west of Germany) with the first line to be commissioned in in the fourth quarter of 2023. The first line of biomethane production will run on 485,000 t/a of chicken dry manure, turkey, horse, duck manure, cow dung, and solid fraction of cattle and pig manure – the manure can be even separated on the agricultural farms in the region by the plant operator nordfuel GmbH. Later, the total substrate amount should be 1,000,000 t/a of dung and manure. The upgrading capacity will be 7,400 m^3_{STP}/h with the annual feed-in of 690 GWh of biomethane. Part of the produced biomethane will be injected into the gas grid, one further part will be compressed and used as CNG in the company's own delivery fleet and the main part of the produced biomethane will be liquefied to 45,000 t/a of bio-LNG. In addition, 8,000 t of ammonia will be separated during the digestate treatment and intended to be supplied to the chemical industry, whereas the solid digestate fraction will be pelletised to 100,000 t/a of digestate pellets.

In parallel to that, 103,000 t/a of biogenic CO_2 will be produced in two different qualities – food-grade CO_2 and CO_2 for industrial applications. Depending on the quality, the produced CO_2 can be potentially used in the chemical industry or for the production of dry ice. An additional possibility for valorisation of 90,000 t/a of biogenic CO_2 is provided by the fact of an announced plant for production of 60,000 t/a of e-methanol for the maritime sector representing renewable fuel of non-biological origin (RFNBO). The announced facility is being planned in Friesoythe near the c-Port with the commissioning date in the 4th quarter of 2027. The planned electrolyser capacity for generation of green H_2 for e-methanol production can be amounted to 85 MW_e, while the required renewable energy should be supplied locally. The key data is, however, subject to change until the end of 2024 in accordance with the final investment decision (Probiotec GmbH, 2021; nordfuel, 2023; top agrar, 2023; Hy2gen, 2023).

3.5. Future opportunities of biogenic CO_2 valorisation in Europe

In the light of the pronounced climate neutrality in the EU by 2050 and the required defossilisation of industrial sectors, the production of biogas and biomethane with subsequent CO_2 capture and valorisation will continue to increase in the future.

Currently, biogas and biomethane sites are often far away from the industries with CO_2 demand, which might, however, change with the erection of new AD sites with CO_2 capture units or by merging the CO_2 produced at the different biogas and biomethane plant facilities via existing (as in the case of the Netherlands) or to be installed CO_2 pipelines. In combination with decentralised points of sustainable sources of, for instance, H_2 and N_2, small-scale and decentralised CO_2 production facilities from biogas and biomethane might enable creation of new sustainable business models.

With respect to the applied technologies, cryogenic separation plays to date a minor role (only 1 % of the applied biogas upgrading technologies in Europe in 2021). However, the importance of cryogenic upgrading may increase with supra-regional CO_2 utilisation or for cold CO_2 applications such as dry ice or CO_2 blasting. In this respect, the results of the overall evaluation including techno-economic assessment as well as GHG balances of the innovative biomethane processes – carried out at the end of the SEMPRE-BIO project – will show whether and under what conditions cryogenic upgrading can provide methane and biogenic liquid CO_2 more efficiently and cost-effectively than conventional processes.

The trend of bio-LNG production and CO_2 valorisation in Europe will continue in the future according to the announced production capacities by 2025 in Germany, Italy, and the Netherlands.

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The change towards the production of high-value biogenic CO_2-based products is not yet apparent, according to the announced and available targets. If biogenic CO_2 becomes scarcer, the competition for CO_2 worth transporting will increase. The competitive advantage of biogenic CO_2 from biogas and biomethane upgrading in comparison to its fossil-derived counterpart comprises proximity to customers, local and biogenic origin, green labelling, high purity grades, almost complete absence of impurities, safeguarded projected supply amounts, and possibility of the fixed non-seasonal price. The utilisation of CO_2 derived from biogas and biomethane with the greatest willingness to pay will then determine the price of this CO_2, while other types of valorisation may have to rely on the sub-segment of other sources. It can be expected that the highest prices for biogenic CO_2 will then be paid for the production of high-value CO_2-based products.

The newly commissioned applications with low quality requirements (CO_2 as essential cost-relevant production factor for the production of algae, e-methanol, SNG from H_2 and CO_2, perhaps new greenhouses) will have specific advantages (even with increasing competition for biogenic CO_2) to use CO_2 from unpressurised or low-pressure upgrading, or simultaneously from smaller plants.

In individual cases as a part of portfolio diversification strategy, fossil-owned stakeholders are taking over the field of valorisation of CO_2 from biogas in the context of the general switch towards renewables. As shown in section 3.4, this is, for instance, true for Danish Nature Energy Biogas A/S, which is the largest biogas producer in Denmark and was acquired by Shell Petroleum NV in September 2023. In Norway in the autumn 2020, Shell's gas distributor Gasnor acquired 50 % of the shares in Renevo AS producing bio-LNG, biogenic CO_2, and biofertiliser. This trend may continue in the future.

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4. Outlook

The defossilisation of industrial sectors can be achieved by replacing CO_2 of fossil origin by its biogenic counterpart against the background of the goal of the climate neutrality by 2050 in the European Union as stipulated by the European Climate Law. The biogenic sources of CO_2 are to be preferred to flue gases from the fossil power plants – in case of CO_2 from biogas not only from the sustainability point of view but also due to the lower energy demand which is needed to capture this biogenic (food-grade) CO_2. Already today, the utilisation of the entire biomethane process chain including CO_2 valorisation for material and/or energy recovery results in ecological and cost benefits.

Within the Net-Zero Industry Act, sustainable biogas/ biomethane technologies are defined as strategic and critical with relevant contribution to decarbonisation and competitiveness "for EU's path towards its 2030 climate and energy objectives" (European Commission, 2023a). In this respect, it would be meaningful to rate the capture of CO_2 representing a by-product from biogas and biomethane production and valorisation of this biogenic CO_2 to value-added products as further strategic net-zero technology.

There are different CO_2 valorisation routes ranging from the well-established to those still to be explored. The production of urea via Bosch-Meiser process, methanol via catalytic CO_2 hydrogenation, methane via CO_2 methanation, concrete curing, CO_2-derived polycarbonates and polyols represent mature technologies. In addition to that within the scope of envisaged work in the SEMPRE-BIO project, the production of value-added products such as biopolymers, biochemicals and alternative sources of protein from biogenic CO_2 represents an innovative route to be demonstrated by the project partner UVIC.

For the future course of the SEMPRE-Bio project, the follow-up on monitoring of further CO_2 valorisation from biogas and biomethane in Europe with support of the SEMPRE-BIO project partners is aspired. Depending on that, the interactive mapping of biogas and biomethane facilities with biogenic CO_2 valorisation can be made publicly available and be updated on the website of SEMPRE-BIO (https://sempre-bio.com/), representing the part of WP 6 Connect, communicate, exploit, replicate in consultation with DBFZ. In addition for 2024, a review paper on CO_2 valorisation from biogas and biomethane is in discussion. In this respect, the participating project partners, external biomethane stakeholders and specific contents and outcomes are to be defined.

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Annex

Questionnaires on status quo of biogas and biomethane plants with CO_2 valorisation in Europe

Objective	Identification and localisation of current biomethane **facilities with CO2 utilization in the EU**, their status (in operation, at the planning stage, demonstration, lab scale) and type of CO2 valorization and several plant parameters (if available))
Questions	Do you have information on biomethane plants **with CO2 utilization**? Please fill in the parameters you have the information on (location, capacity, type of CO2 utilization).
How to manage this sheet /comments	copy the table or sheet in case you have more the information on more than one plant; choose type or amount; the abbreviation "m3 STP /h biomethane" means "standard temperature and pressure (the normal state at 0 °C and 1013.25 mbar)"

Parameter	*Type*	*Amount*	*Unit*
Biogas upgrading facility			
Country			
Location			
Company name			
Status			
Year of initial plant operation			
Upgrading capacity			m^3_{STP}/ h biomethane
Installed electrical power			kW_e
Upgrading technology			
Raw gas production			m^3_{STP}/ a
CH_4 production			m^3_{STP}/ a
Substrate 1			t/ a
Substrate 2			t/ a
Substrate 3			t/ a
Substrate 4			t/ a
Substrate 5			t/ a
Comments			
Weblink further information			
CO_2 valorization *(please refer to the options in the table right hand)*			
Year of initial CO_2 utilization			
CO_2 production per facility			t/ a
CO_2 utilization sector 1			t/ a
CO_2 utilization sector 2			t/ a
CO_2 utilization sector 3			t/ a
CO_2 utilization sector 4			t/ a
CO_2 utilization sector 5			t/ a
Company name CO_2 utilization 1			
Company name CO_2 utilization 2			
Company name CO_2 utilization 3			
Company name CO_2 utilization 4			
Company name CO_2 utilization 5			
Comments			
Weblink further information			

Figure 13: Questionnaire 1 on status quo of plants with CO_2 valorisation in Europe (source: DBFZ, 2023)

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Objective	Identification of **innovative biomethane plants in EU Member States** (kind of technology, location, capacity, current substrats used for biomethane production), facilities with/without CO2 utilization, illustration in a map
Questions	Do you have information about **innovative biomethane** plants in your country? Please fill in.

Parameter	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6	Plant 7	Plant 8
Country								
Location /site								
installed electrical capacity, MW_e								
raw gas production, m^3/a								
biomethane production (CH4), m^3_{STP}/a								
feed-in capacity biomethane, m^3_{STP}/h								
type of innovative technology								
type of substrates								
CO_2 valorization - yes/no								
CO_2 production per facility, t/a								
CO_2 utilization sector								
Comments								
Weblink further information								

Figure 14: Questionnaire 2 on status quo of plants with CO_2 valorisation in Europe (source: DBFZ, 2023)

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DBFZ literature overview, 2023: listing of literature sources for biogas and biomethane plants with CO_2 valorisation in Europe in alphabetical order

Table 4: Listing of literature sources as collected during the DBFZ literature research, 2023 for biogas and biomethane plants with CO_2 valorisation (currently in operation and to be commissioned by the end of 2023) and in the planning stage in Europe; the specific citation provided in the list of literature

Operational status	Literature sources in alphabetical order
Biogas and biomethane plants with CO_2 valorisation (currently in operation and to be commissioned by the end of 2023)	A.F. Bioenergie, 2021; Apsley Farms, 2023; ArgoviaToday, 2023; Association d'Initiatives Locales pour l'Energie et l'Environnement, 2021; baden online, 2015; Baraldo Costruzioni, 2023a; Biogas-E, 2018; BiogasWipptal, 2023; Bioman, 2023; Biovalue, 2023b; Bright Renewables, 2018; Bright Renewables, 2023b; Bright Renewables, 2023c; Bright Renewables, 2023d; Carbon Capture Scotland Limited, 2022; Cavac, 2021; Caviro Extra, 2023; Commune di Reggio Emilia, 2023; Consorzio Biogas, 2020; Cordis, 2023; Cryo Pur, 2017; Cryo Pur, 2023; den Heijer, N.; Coenradie, A., 2017; Dumont, 2015; EcoFuels, 2023; EE News, 2013; Electrochaea, 2023; energie bewegt Winterthur, 2023; Energie Expertisecentrum Flevoland, 2023; Enomondo, 2023; EnviTec Biogas, 2023a; EnviTec Biogas, 2023b; Esposito et al., 2019; European Biogas Association, 2023; Farmers Weekly, 2023; Flevozine, 2017; Forest Heath District Council, 2015; FreshPlaza, 2022; Gasworld, 2014; Hitachi Zosen INOVA, 2022b; Hitachi Zosen Inova, 2023a; Hy2gen, 2023; Hydrogen24, 2022; IEA Bioenergy Task 37, 2017; IEA Bioenergy Task 37, 2020; IEA Bioenergy Task 44, 2021; Iren, 2023; Landbouw- en Biogasbedrijf Kloosterman, 2023; Limeco, 2022; Limeco, 2023; Malmberg, 2023; Material Change, 2023a; Material Change, 2023b; Miimosa, 2023; Mikunda et al., 2015; Money Controller, 2022; Nippon Gases, 2022; Nippon Gases, 2023; nordfuel, 2023; Nordsol, 2023a; Novamont, 2020; Østfoldforskning, 2020; Pentair, 2014; Pentair, 2016; Pentair, 2017; Pentair, 2020; Pentair, 2022a; Pentair, 2022b; Pentair, 2023; Peters Biogas, 2023; PFI Biotechnology, 2023; Probiotec GmbH, 2021; Process Industry Informer, 2022; Quotidiano Piemontese, 2022; Reklima, 2023; Renevo, 2022b; Rijksdienst voor Ondernemend Nederland, 2010; Ruhe Biogas, 2023; Schlautmann et al., 2021; Società Chimica Italiana, 2022; Spee, 2016; Store and Go, 2019; Sustainable Bourne Valley, 2023; Sustainable Fuel Plant, 2023a; Swisspower, 2019; Swisspower, 2022; The Herald, 2021; Thyssengas, 2021; top agrar, 2023; Vale Green Energy, 2023a; Vale Green Energy, 2023b; Verdemobil Biogaz, 2023a; Wabico, 2022; Waternet, 2023; World Biogas Association, 2020
Biogas and biomethane plants with CO_2 valorisation in the planning stage	Acorn Bioenergy, 2022b; Acorn Bioenergy, 2023a; Acorn Bioenergy, 2023b; Acorn Bioenergy, 2023c; Afval Online, 2023; Ahmadi and Avila-Lopez, 2022, Andover Advertiser, 2022; Attero, 2023; Baraldo Costruzioni, 2023b; Bayerische Ingenieurekammer-Bau, 2023; Bezirksregierung Münster, 2022; Bioenergy Insight, 2022a; Bioenergy Insight, 2022b; Biogas Bree, 2023; Biogas Neuburg Steinhausen, 2022; Biovalue, 2023a; Bright Renewables, 2023a; Building Supply, 2021; bwe Energiesysteme, 2023; DBG Bio Energy, 2022; EccodalleCitta, 2021; Eichenhof Energie, 2023; ENGIE BiOZ, 2021; EnviTec Biogas, 2022; Evenley Parish Council, 2022; Gaz de Bordeaux, 2022; Geestferkel, 2023; gwf Gas + Energie, 2023; Hitachi Zosen INOVA, 2022a; Hitachi Zosen Inova, 2023b; Hitachi Zosen Inova, 2023c; iLaks, 2021; Innovacjon Norge, 2023; Ixora Energy, 2022; Ixora Energy, 2023; Krieg & Fischer Ingenieure GmbH, 2023; Kvinnheringen, 2023; Landkreis Schwandorf, 2021; Made in, 2023; MVV Umwelt 2023; Nordsol, 2023b; Nordsol, 2023c; NTB Kommunikasjon, 2022; NTB Kommunikasjon, 2023; Onetz; 2020; Perpetual Next Conversions, 2023; Renevo, 2023, SAS GAZTEAM ENERGIE, 2022; Scapigliato, 2021; Scapigliato, 2023; Schwelm, 2023; SESA, 2023; Società Chimica Italiana, 2022; Solagro, 2023; Sømna Biogass Eiendom, 2022; Sustainable Fuel Plant, 2023b; The Press and Journal, 2023a; The Press and Journal, 2023b; top agrar, 2022, Tysoe Parish Council, 2022a; Tysoe Parish Council, 2022b; Veas, 2023, Verdemobil Biogaz, 2023a; Wärtsilä, 2019; Winchester Action on Climate Change, 2022

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Overview of the biogas and biomethane plant sites with CO_2 valorisation (current and expected by the end of 2023) in Europe (commercial-scale CCU)

Table 5: Biogas and biomethane plant sites with CO_2 valorisation (current and expected by the end of 2023) in Europe (commercial-scale CCU), differentiated by commissioning year of CO_2 capture unit, utilised substrates for AD, bio-LNG production capacity in tonnes per day (t/d) or per year (t/a), if applicable, CO_2 production capacities in kilogram per hour (kg/h) or tonnes per year (t/a), type of CO_2 utilisation and CO_2 food-grade quality, if indicated as of 10/2023 (source: based on DBFZ literature review, 2023; DBFZ survey of 4 Horizon Europe projects on biomethane, 2023; DBFZ survey of the German biomethane plant operators, 2023)

Place	Commi-ssioning year of CO_2 capture unit	Substrates	bio-LNG production (if applicable)	CO_2 production capacity[4]	CO_2 valorisation sector	food-grade CO_2 (if indicated)	Country[5]
Merksplas	2018	garden, fruit and vegetable waste	-	554 t/a	greenhouse farming	yes	BE
Nesseln-bach	2023	food waste	-	3,500 t/a	food and beverage industry	yes	CH
Dietikon	2022	wastewater	-	n.a.	energy production		CH
Zuchwil	2019	wastewater	-	n.a.	energy production		CH
Güstrow	2023	chicken manure, energy crops	9,600 t/a	15,000 t/a	greenhouse farming, food and beverage industry	yes	DE
Krefeld	2022	sewage sludge	-	879 t/a	industrial gas applications	yes	DE
Friesoythe	2023	(solid fraction) manure, cow dung	45,000 t/a	103,000 t/a	energy production, industrial gas applications	yes	DE
Darchau	2023	manure, cattle slurry, grass from floodplains	900 t/a	1,900 t/a	not specified		DE

[4] n.a. = not available

[5] BE = Belgium, CH = Switzerland, DE = Germany, DK = Denmark, FR = France, IT = Italy, NL = the Netherlands, NO = Norway, UK = the United Kingdom (including Scotland and Northern Ireland)

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Werlte	2013	residual and waste materials	-	n.a.	energy production		DE
Pirmasens	2016	energy crops	-	n.a.	energy production		DE
Augsburg	2020	organic waste	-	4,523 t/a	industrial gas applications		DE
Esbjerg	2019	manure, animal bedding, food waste, industrial and retail residues, energy crops	-	16,250 t/a	food and beverage industry, industrial gas applications	yes	DK
Hvidovre	2016	sewage sludge/ raw biogas from AD, pure CO_2 stream from biogas upgrading	-	n.a.	energy production		DK
Valenton	2015	sewage sludge	1 t/d	67 kg/h	not specified	yes	FR
Strasbourg	2016	sewage sludge	-		not specified		FR
Poiré-sur-Vie	2022	manure, agricultural and agri-food co-products	-	3,700 t/a	greenhouse farming	yes	FR
Machecoul	2020	cattle slurry, straw manure, (intermediate) energy crops, market garden waste	-	2,500 t/a	greenhouse farming	yes	FR
Bernadets-Debat	2022	livestock manure, crop waste	-	3,700 t/a	greenhouse farming	yes	FR
Reggio Emilia	2023	organic waste, wood cellulose vegetable waste	-	10,000 t/a	food and beverage industry, industrial gas applications	yes	IT

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Pfitsch	2022	bovine waste, bovine liquid manure	4,000 t/a	7,000 t/a	food and beverage industry	yes	IT
Montello	2017	organic fraction of municipal solid wastes	-	7,000 t/a	not specified	yes	IT
Candiolo	2020	slurry, manure, intermediate crops	2,000 t/a	4,000 t/a	food and beverage industry, industrial gas applications	yes	IT
Faenza	2020	winemaking by-products and wastewater	9,000 t/a	7,000 t/a	food and beverage industry	yes	IT
Lugo	2019	agricultural by-products, non-food materials, algae	yes	n.a.	not specified		IT
Bottrighe	2020	by-products sugars fermentation	-	n.a.	industrial gas applications		IT
Barbarano Mossano	2022	dairy by-products	yes	n.a.	food and beverage industry	yes	IT
Maniago	2020	kitchen scraps, green maintenance, fruit waste	-	n.a.	greenhouse farming, food and beverage industry	yes	IT
Well	2011	vegetable waste, expired foodstuffs	-	2,000 t/a	greenhouse farming, industrial gas applications	yes	NL
Amster-dam	2021	expired products from supermarkets	3,400 t/a	6,300 t/a	greenhouse farming		NL
Amster-dam	2021	sewage sludge	-	10,534 t/a	greenhouse farming		NL
Luttel-geest	2017	manure, residual food mix	-	n.a.	greenhouse farming		NL

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Westdorpe	2019	manure, organic residual materials	-	20,000 t/a	greenhouse farming, industrial gas applications	yes	NL
Alphen aan den Rijn	2014	vegetable fruit and garden waste	-	1,797 t/a	greenhouse farming, industrial gas applications	yes	NL
Weurt	2012	vegetable fruit and garden waste	-	3,000 t/a	greenhouse farming	yes	NL
Waalwijk	2015	roadside grass, vegetable waste, flotation sludge, unpacked supermarket waste	-	600 kg/h	not specified	yes	NL
Almere	2017	roadside grass, manure, grain and corn residues, beet tips	-	600 kg/h	greenhouse farming	yes	NL
Wijster	2014	organic fraction from residual waste	177 kg/h pilot	620 kg/h	greenhouse farming	yes	NL
Tirns	2012	not specified	-	n.a.	industrial gas applications	yes	NL
Nieuwe-roord	2012	maize silage, vegetable residues	-	4,000 t/a	food and beverage industry	yes	NL
Stord	2022	cattle manure, salmon farming waste, fish sludge	8 t/d	417 kg/h	food and beverage industry, industrial gas applications	yes	NO
Sem	2018	food waste, livestock manure, industrial waste	-	394 t/a	greenhouse farming		NO

Newtown-stewart	2019	cattle slurry, farm silage waste, dairy sludge, fruit and vegetables from retailers	3.2 t/d	900 t/a	industrial gas applications		UK
Hampton Bishop	2016	cattle and chicken manure, apple pomace, maize silage	-	850 kg/h	not specified	yes	UK
Pershore	2013	grass, maize, sugar beet, wheat	-	3,000 t/a	greenhouse farming	yes	UK
Throckmor-ton	2015	energy crops	-	1,420 kg/h	food and beverage industry	yes	UK
Arreton	2014	maize and grass silage, break crops	-	6,900 t/a	industrial gas applications	yes	UK
Birching-ton	2015	energy crops	-	550 kg/h	not specified	yes	UK
Birching-ton	2016	energy crops	-	980 kg/h	not specified	yes	UK
Red Lodge/ Worlington	2016	maize, sugar beet, agricultural by-products, manure	-	894 kg/h	greenhouse farming, food and beverage industry	yes	UK
Helmdon	2016	maize, rye and grass silage	-	891 kg/h	food and beverage industry, industrial gas applications	yes	UK
Euston	2016	energy crops	-	842 kg/h	not specified	yes	UK
Andover	2016	maize and rye silage	-	1,600 kg/h	food and beverage industry, industrial gas applications	yes	UK
Crocket-ford	2022	(cattle) manure, poultry litter,	-	n.a.	industrial gas applications	yes	UK

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		energy crops, whey, distillery by-product liquid feeds					