ANALYSIS OF BIO-CO_2 STREAMS FOR METHANOL SYNTHESIS

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ABSTRACT: Bio-CO_2 streams in conjunction with renewable hydrogen present a promising pathway for the production of maritime methanol. However, impurities present in those streams might affect the catalyst employed in the methanol synthesis process. This study aims to characterize the impurity profiles of biogenic CO_2 from biogas plants to develop a targeted pre-treatment strategy enabling its potential use in methanol synthesis. To this end, sampling campaigns were conducted at actual biogas plants, which present a promising bio-CO_2 source, whereas a membrane gas absorption unit was deployed to capture and purify to a certain extent the bio-CO_2 stream. The composition of bio-CO_2 feedstocks is evaluated, as contaminants can lead to pipeline corrosion during transportation and cause catalyst deactivation through poisoning. Results showed effective capture efficiency and significant impurity reductions, whereas chloride compounds identified as the primary residual contaminant requiring downstream treatment before the synthesis process.
Keywords: bio-CO_2, campaigns, CO_2 capture, DEA, impurities, methanol, marine fuels

1 INTRODUCTION

For over a decade, the International Maritime Organization (IMO) has prioritized the reduction of emissions from the shipping sector, targeting pollutants such as of sulphur oxides (SO_x), nitrogen oxides (NO_x), and particulate matter (PM). In 2018, the IMO adopted a strategy aimed at reducing total annual greenhouse gas (GHG) emissions from international shipping by 50% by 2050, relative to 2008 levels. Particularly, the strategy targets to "reduce CO_2 emissions per transport work, on average across international shipping, by at least 40 percent by 2030, pursuing efforts towards 70 percent by 2050, compared to 2008". This regulatory framework has become a key driver in as a major driving force for the adoption of alternative marine fuels, including methanol [1].

Methanol is considered a promising fuel for meeting maritime emission regulations. Compared to heavy fuel oil (HFO), commercially available methanol can reduce nitrogen oxide (NO_x) emissions by up to 80%, sulphur oxides (SO_x) by 99%, and particulate matter (PM) by 95%. When used in combination with advanced engine technologies, methanol could potentially enables compliance with the IMO's stringent emission standards) [2]. At present, methanol is available at more than 120 ports worldwide and is traded globally, with over 90 production facilities collectively offering an annual production capacity of approximately 120 million tons. However, the carbon intensity of methanol is closely dependent on the feedstock and the production pathway employed. When considering well-to-propeller emissions, e-methanol ranks among the lowest-emission fuel options for maritime transport [1].

e-Methanol could be produced through CO_2 hydrogenation, which involves the catalytic conversion of bio-derived CO_2 and green hydrogen into methanol [3]. Biogenic CO_2 emissions refer to those that occur naturally within the carbon cycle and are generated by upstream processes involving organic materials, such as combustion, fermentation or anaerobic digestion. Potential industrial sources of bio-CO_2 include biogas/biomethane plants, bioethanol, food and beverage as well as biomass combustion and pulp and paper plants. This sector is inherently distributed and is characterized by variations in geographical location, plant scale and CO_2 purities. A key challenge lies in the presence of impurities within the CO_2-rich streams which vary based on the type of biomass and the processing technology employed [4].

These variations influence the chemical pathways and by-products generated during processing, thereby resulting in CO_2 emissions with diverse compositional characteristics [5]. Commonly detected impurities include sulphur species (e.g. H_2S, SO_2), halogens (e.g. HCl, HF), volatile organic compounds (VOCs), siloxanes and heavy metals traces [4]. These contaminants significantly affect CO_2 purification requirements, as they can poison methanol synthesis catalysts, promote equipment corrosion, and reduce overall process efficiency [6], [7]. Therefore, to enable the production of e-methanol, appropriate conditioning must be implemented and maintained throughout each stage of the CO_2 supply chain. Once the impurities profile is known, particular attention must be paid to ensure compliance with stringent specifications for CO_2 capture, transport, and final utilization as a feedstock in methanol synthesis.

To address the above challenge, the EU-funded project M^2ARE (Grant Agreement No. 101136080) is investigating the use of bio-CO_2 resources in combination with renewable H_2 for the production of methanol specifically intended for maritime applications. In this framework, the present study focuses on the analysis of impurity profiles at selected biogas sites through targeted sampling campaigns, with the ultimate objective of designing an efficient gas cleaning strategy prior to methanol synthesis. Membrane gas absorption (MGA) is an efficient technology for separating specific gases, such as CO_2, from mixed streams. By combining a selective membrane with liquid absorbent, MGA, enables targeted removal of contaminants with high efficiency and a compact system design, making it well-suited for biogas purification and other industrial applications.

The structure of this work is as follows. Section 2 details the experimental procedure carried out during sampling campaigns at biogas facilities, aimed at characterizing the impurities present in CO_2 flue gas streams whereas the MGA unit was employed on-site for CO_2 capture. Section 3 presents the results obtained from the sampling campaigns. Finally, Section 4 summarizes the conclusions and outlines perspectives for future work.

2 EXPERIMENTAL METHODOLOGY AND FIELD IMPLEMENTATION

To establish accurate reference data on the impurity profile of bio-CO_2 sources, two biogas facilities were selected for investigation. These facilities operate combined heat and power (CHP) plants fuelled by biogas, each with a nominal capacity of approximately 12,000 m^3 per day and a maximum production capacity of up to 18,000 m^3 per day. The primary feedstock consists of agricultural residues, which are subject to seasonal variability. Nevertheless, the biogas stream exhibits a relatively stable composition, with methane (CH_4) content maintained at approximately 60 ±2% and carbon dioxide (CO_2) content at approximately 36 ±1%.

2.1 Sampling procedures at biogas plants

During the sampling campaigns, two sequential measurement activities were carried out: one focused on the analysis of the bio-CO_2 gaseous stream, and the other on the evaluation of the membrane-based CO_2 capture system. Both streams underwent comprehensive analysis to determine their chemical composition and to identify key impurities of concern. The sampling point was strategically located downstream of any existing gas purification units (e.g. DeSOx systems for H_2S removal) and upstream of the biogas utilization unit for electricity generation (e.g. CHP unit).

Raw gas samples were collected at a designated sampling point using gas sampling bags and subsequently transported for off-site analytical characterization. The primary objective of these measurements was to determine the impurity composition of the biogas, with particular emphasis on the detection of trace levels of siloxanes. In addition to sulphur compounds, siloxanes are well-documented in the literature as among the most prevalent impurities in biogas streams, often occurring at appreciable concentrations.

Membrane Gas Absorption (MGA), an absorption process that employs hollow fiber membranes as the contacting interface between gas and liquid phases, was implemented on-site at the selected bio-CO_2 industrial facilities for CO_2 capture and purification. In this configuration, the gas mixture is introduced on the lumen side of the hollow fibres, while a CO_2 capture medium (solvent) flows along the shell side, either co-currently or counter-currently, enabling selective absorption of CO_2 via chemical binding. In this study, aqueous solution of 2M Diethanolamine (DEA) was used as the absorption solvent. The presence of a reactive solvent is essential for achieving high CO_2 transfer rates through the membrane, as the chemical reactions significantly enhance mass transfer. The membrane serves to provide efficient contact between the gas and liquid phases while preventing phase mixing, thereby maintaining a strong driving force and improving overall mass transfer performance. This synergistic combination results in an intensified and compact separation process, offering a significant reduction in equipment volume compared to conventional absorption columns [8]. The MGA pilot unit consists of a 2.5×8 Liqui-Cel™ 3M EXF membrane contactor, designed for a max liquid flow rate of 0.7 m^3/h. The system is complemented by ancillary components, including feed, mixing and disposal tanks, fluid connectors, pumps and measurement instrumentation.

The experimental procedure was conducted through a series of systematic steps, as schematically illustrated in Figure 1. Initially, the liquid solvent was prepared and loaded into the storage tank. Subsequently, the composition and total flow rate of the feed gas were carefully analysed and recorded. Both gas and liquid streams were then introduced into the membrane module, with the liquid pressure maintained approximately 0.1 to 0.5 bar higher than the gas side, ensuring that no biogas dispersion will occur into the liquid phase. Throughout the experiment, real-time monitoring of the gas effluent composition and total flow rate was performed using an Online Infrared Biogas Analyser (Gasboard-3200), with measurement ranges of CH_4: 0-100%, CO_2: 0-50%, H_2S: 0-9999 ppm, and O_2: 0-25%. In addition, the influence of key process parameters, such as the gas-to-liquid (G/L) ratio, was systematically investigated to assess their effect on overall process performance. The absorption process was operated continuously until the DEA solution reached saturation, as defined by the equilibrium CO_2 loading capacity of the solvent. The MGA campaign was carried out over a sampling duration exceeding 2 hours. Upon solvent saturation, liquid samples were collected for subsequent ex situ analysis.

Table I and II present the general characteristics of the membrane system and the experimental conditions under which the tests were conducted.

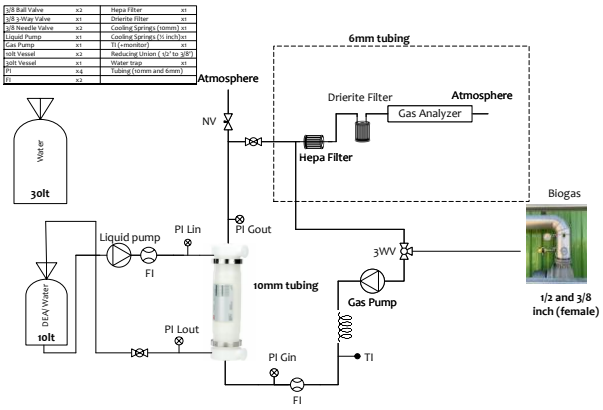


Figure 1: Flow diagram of capturing system in biogas campaigns.

Table I: Technical characteristic of the 2.5×8 Liqui-Cel™ 3M EXF membrane contactor.

Contactor	Extra flow 2.5×8
Effective membrane area (cm^2)	14,000
Cartridge configuration	Cross-flow
Fibre ID/OD (cm)	0.024/0.03
Fibre material	Polypropylene
Fibre porosity (%)	40
Fibre pore size (μm)	0.03
Number of fibres	10,000
Length (cm)	27.7
Diameter (cm)	7.7

Table II: Experimental conditions in biogas campaigns.

Parameters	Biogas plant	
	No. 1	No. 2
Sample conditions		
Pressure [mbar]	80	115
Temperature [°C]	20	23

MGA upstream Feed		
Pressure [mbar]	150	150
Temperature [ºC]	22	30.5
Flow [L/min]	16	16
Absorption solvent-DEA		
Pressure [bar]	0.2	0.2
Temperature [ºC]	20	23
Flow [L/min]	2.5	2.5
Concentration [M]	2	2

Sampling and analysis were essential for understanding the composition characteristics of the CO_2 stream. It was critical to ensure that the absorption solution collected during the tests accurately reflected a CO_2 stream suitable for methanol synthesis following the capture-desorption process.

A screening of selected trace elements was performed to evaluate their presence and assess their potential impact on the downstream processing chain, with particular emphasis on the following elements:

- Chlorides (Cl^-)
- Fluorides (F^-)
- Sulphides (S^{-2})
- Sulphur oxide (SO_4^{-2})
- Arsenic (As)
- Mercury (Hg)
- Antimony (Sb)

To this end, appropriate and standardized analytical methods were employed to guarantee consistency and reproducibility of the results. The selected methodologies are summarized in Table III. These methods were selected to ensure that the sampling and analysis procedures followed established protocols and best practices in the field. This allowed for reliable data interpretation and meaningful conclusions to be drawn from the study.

Table III: Standards for sampling and analysis.

Parameters	Analytic method	Threshold
Chlorides (Cl^-)	SMEWW-4500	0.004
Fluorides (F^-)	SMEWW-4500	$7.89x10^{-4}$
Sulphides (S^{2-})	ISO10530:2002	$1.58x10^{-4}$
SO_4^{2-}	SMEWW-4500	0.0789
Arsenic (As)	ASTM D2972-03	$3.95x10^{-5}$
Mercury (Hg)	ASTM D3223:2000	$7.89x10^{-6}$
Antimony (Sb)	ISO 15586:2003	$7.89x10^{-5}$

3 RESULTS OF IMPURITY CHARACTERIZATION IN BIOGAS FACILITIES

The analytical results are categorized into two groups: (i) those reflecting the composition of the raw flue gas stream prior to CO_2 capture, and (ii) those representing the composition of the gas stream following the absorption process. This distinction enables a comparative evaluation of impurity behaviour throughout the gas capture stage. The first set of results corresponds to the untreated flue gas composition, measured upstream of the CO_2 capture unit.

The analysis of the biogas streams from both facilities revealed a consistently high methane content, accompanied by low oxygen levels and well-controlled hydrogen sulphide (H_2S) concentrations. Notably, Plant No. 1 did not exhibit detectable sulphur-containing compounds, with H_2S levels measured at 0 ppm. In contrast, Plant No. 2 showed slightly elevated H_2S concentrations, which may pose challenges for downstream processing, particularly in methanol synthesis. The detailed composition of the flue gas streams from both facilities is presented in Table IV.

In addition, an analysis was conducted to detect the presence of siloxane species in the CO_2 stream. The calibrated data for siloxanes revealed consistent contaminant profiles across both plants, with concentrations falling below the quantification limits. The absence of detectable siloxanes in the biogas streams may be attributed to the nature of the feedstock. Since biogas facilities typically experience seasonal variability in feedstock composition, this observation should not be considered conclusive. During the sampling campaign, the feedstock primarily consisted of agricultural residues, a condition under which siloxane content is typically low. This finding is consistent with the results reported by Piechota et al. who observed reduced siloxane concentrations in biogas derived from agricultural sources [9]. The measured values for each siloxane species are presented in Table V.

Table IV: Composition of flue gas stream in biogas campaigns.

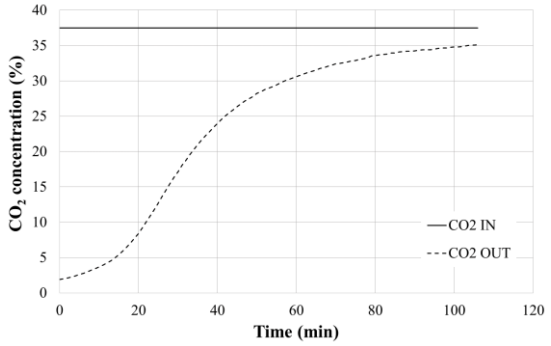
Component	Biogas plant	
	No. 1	No. 2
CH_4 (% vol)	60.2	61.7
CO_2 (% vol)	37.5	38.2
O_2 (% vol)	0.3	0.1
H_2S (ppm)	0	20.0-30.0

Table V: Detected siloxane species and their limit concentration in biogas/flue gases streams.

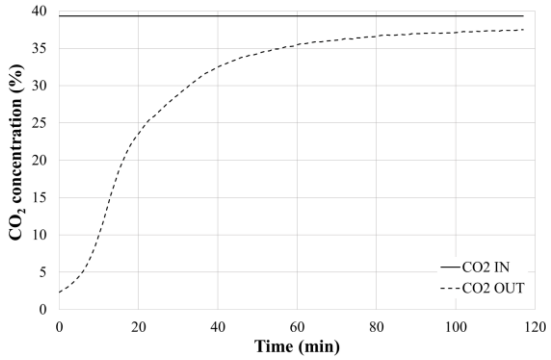
Findings	Result	Threshold [ppmv]
Tetramethylsilan	Below thres-hold	0.02771
Trimethylsilanol		0.02771
Hexamethyldisolxan		0.01506
Hexamethylcyclotrisiloxan		0.01099
Octamethyltrisiloxan (L3)		0.01034
Octamethylcyclotetrasiloxan		0.00824
Decamethyltetrsiloxan (L4)		0.00824
Decamethylcyclopentasiloxan		0.00659
Total silicon (calc.)		0.00379
Sum of silicon organic compounds		0.00139
Sum SiO_2		0.0407

The experimental results from the MGA campaign are presented in the following figures, illustrating the variation of CO_2 concentration in the gas stream downstream of the MGA unit over time, as well as the corresponding CO_2 loading capacity of the absorption solvent. After approximately two hours of continuous operation, the CO_2 concentration downstream of the MGA unit gradually approached its initial upstream value, indicating that absorption equilibrium has been reached. The CO_2 loading capacity of the aqueous DEA solution is defined as the ratio of moles of CO_2 absorbed to moles of DEA. Under standard absorption conditions, typical CO_2 loading capacity for DEA ranges between 0.4 and 0.5 mol CO_2/mol DEA. While the theoretical maximum capacity

is 1 mol CO_2/mol DEA, practical limitations, such as reaction kinetics, solution viscosity, and equilibrium constraints determined by operating temperature and CO_2 partial pressure, often reduce achievable values. In the case of Biogas Plant No. 1, the 2 M DEA solution achieved a CO_2 loading capacity exceeding 0.8 mol CO_2/mol DEA under the given conditions. At Plant No.2, the same solution reached a loading capacity above 0.6 mol CO_2/mol DEA under identical operating parameters.

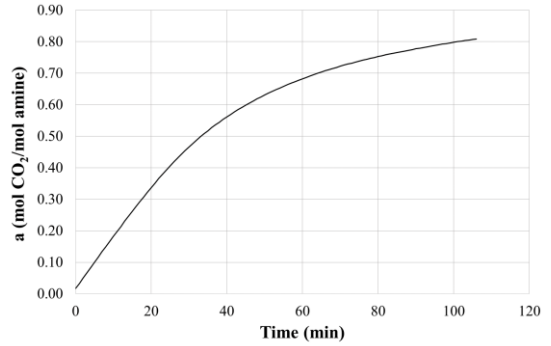


(a)



(b)

Figure 2: CO_2 concentration variation in the gaseous stream after MGA with time (a- Biogas plant No.1, b-Biogas plant No.2).



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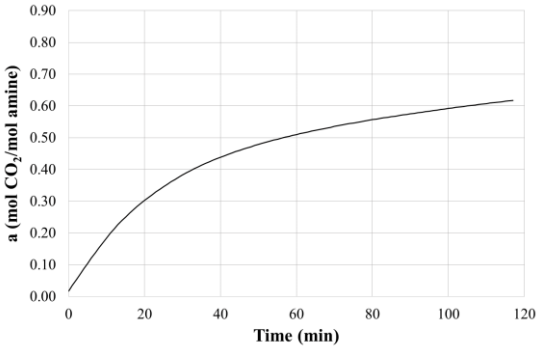

(b)

Figure 3: CO_2 absorption loading as a function of time (a-Biogas plant No.1, b-Biogas plant No.2).

The solvent density was measured using the standard test method for determining the density and relative density of liquids with a Digital Density Meter, in accordance with ASTM D4052-18a. The results for both saturated and unsaturated solvent samples are presented in Table VI below.

Table VI: Summary density table for unsaturated and saturated DEA solution for the biogas plants.

Density of 2 M DEA at 25 ºC	**Value [g/mL]**	
Unsaturated	1.0207	
Biogas Plant	No. 1	No. 2
Saturated	1.0744	1.0719

The typical density of an aqueous 2 M DEA solution prior to CO_2 absorption is estimated to range from 1.02 to 1.05 g/cm^3 at room temperature. Upon saturation with CO_2, the density generally increases by approximately 0.02 to 0.05 g/cm^3, resulting in a final density in the range of 1.05 to 1.10 g/cm^3. This variation is influenced by factors such as the concentration of DEA, the degree of CO_2 loading, and the operating temperature.

During experimental analysis, it was observed that the saturated samples had sequestered CO_2 primarily in the form of carbonate ions, as evidenced by strong effervescence upon acid addition. Solution composition analysis was performed using certified reference standards, and quantification was conducted via the method of standard additions to account for potential matrix effects and to enhance analytical accuracy, as previously described. The pure solvent was also analysed to identify any residual impurities that may have resulted from previous operations.

In particular, the analysis from both biogas plant campaigns indicated that chloride removal was the only necessary conditioning step required for the utilization of bio-CO_2 in methanol synthesis. It is the only contaminant in both cases whose concentration could exceed the catalyst's tolerance limit. This conclusion is supported by the compositional and quality data obtained from the study, as presented in Table VII. The maximum concentration reflects a conservative scenario in which the entire volume of captured CO_2 is directed to methanol synthesis without intermediate purification.

Sampling at the selected industrial sites revealed elevated concentrations of chlorides in the CO_2 streams that could potentially harm the methanol synthesis catalyst. To enable the feasible utilization of such streams

for methanol production, it is necessary to consider available processes for effective chloride reduction. Such removal processes could involve methods such as wet scrubbing [10], dry scrubbing [11], and adsorption techniques [12], [13]. The selection of the most appropriate method for the removal of halogenated compounds from a CO_2 stream depends on several factors, including the composition of the gas mixture, the specific operating conditions, and the requirements of downstream processing. Each technology presents distinct advantages in terms of removal efficiency, operational complexity and waste management. Currently, wet scrubbing with alkaline solutions is the most widely adopted approach, effectively removing both elemental and acidic halogen species. Dry scrubbing is preferred in moisture-sensitive applications, while adsorption techniques are particularly suited for the capture of trace amounts of halogenated organic compounds [10], [12], [14].

Table VII: Amounts of traces captured by the amine process expressed as maximum potential concentrations in the CO_2 stream and the reactor inlet stream.
*b.t = below threshold, n.d = not detected

Parameters	**Content (ppm)**			
	Biogas plant No. 1		**Biogas plant No.2**	
	Per CO_2 absorbed	Reactor inlet	Per CO_2 absorbed	Reactor inlet
Chlorides (Cl^-)	16.5	4.1	39.3	9.8
Fluorides (F^-)	$9.95x10^{-3}$	$2.49x10^{-3}$	$5.37x10^{-3}$	$1.34x10^{-3}$
Sulphides (S^{2-})	$9.47x10^{-4}$	$2.37x10^{-4}$	$2.1x10^{-4}$	$5.26x10^{-5}$
SO_4^{2-}	b.t (<0.0789)	b.t (<0.0789)	b.t (<0.0789)	b.t (<0.0789)
Arsenic (As)	n.d	n.d	n.d	n.d
Mercury (Hg)	n.d	n.d	n.d	n.d
Antimony (Sb)	n.d	n.d	n.d	n.d

4 CONCLUSIONS

The scope of this study was to investigate the suitability of bio-derived CO_2 streams from biogas plants as feedstock for e-methanol production targeted at maritime applications. The analysis focused on the impurity profiles of these streams, which vary significantly depending on the type of biomass feedstock and the associated processing conditions. Such impurities pose challenges related to transport safety and catalyst deactivation during methanol synthesis. The deployment of a Membrane Gas Absorption (MGA) unit, using diethanolamine (DEA) as the absorbent, demonstrated effective CO_2 capture and notable impurity reduction, thereby simplifying downstream gas purification requirements. Following the MGA treatment, chloride removal was identified as a necessary step to meet the purity specifications for methanol synthesis. These findings could support the feasibility of decentralized CO_2 purification strategies and emphasize the potential of integrating bio-CO_2 into green methanol production pathways. In continuation of this work, additional sampling campaigns will be conducted at biomass combustion plants to investigate the respective impurity profiles of the bio-CO_2 stream.

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6 ACKNOWLEDGEMENTS

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