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INDUSTRIAL REQUIREMENTS FOR THE MEASUREMENT OF BIOMETHANE CONTENT WITHIN GAS GRIDS

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CONTENTS

ABBREVIATIONS

BSI	British Standards Institution
GHG	Greenhouse Gas
NPL	National Physical Laboratory
NMS	National Measurement System
UK	United Kingdom
PRM	Primary Reference Material
POST	Parliamentary Office for Science and Technology
NTS	National Transmission System
NGP	National Grid Plc
GDN	Gas Distribution Network
IGT	Independent Gas Transporters
AD	anaerobic digestion
BioSNG	Bio-synthetic natural gas
NNFCC	National Non-Food Crops Centre
FES	Future Energy Scenarios
ENA	Energy Networks Association
Ofgem	Office of Gas and Electricity Markets
BEIS	Department for Business, Energy & Industrial Strategy
RHI	Renewable Heat Incentive
REGO	Renewable Energy Guarantees Origin
FIT	Feed-in Tariffs
ROC	Renewables Obligation Certificate
ICS	Independent Certification Schemes
BMCS	Biomethane Certification Scheme
GGCS	Green Gas Certification Scheme
CHP	Combined Heat and Power
BS	British Standards
FMD	Fuel Mix Disclosure
NGN	Northern Gas Networks
WWU	West and Wales Utilities
NEA	Network Entry Agreement
BNEF	Biomethane Network Entry Facility
GC	Gas Chromatography
GS(M)R	Gas Safety (Management) Regulations 1996
GCOTER	Gas Calculation of Thermal Energy Regulations
IGEM	Institute of Gas Engineers and Managers
CCS	Carbon Capture Storage
CV	Calorific Value
LDZ	Local Distribution Zone
FBM	Future Billing Methodology
RTN	Real-Time Networks
CNG	Compressed Natural Gas
LNG	Liquified Natural Gas
HGV	Heavy Goods Vehicles
DfT	Department for Transport
RTFO	Renewable Transport Fuel Obligation
RTFC	Renewable Transport Fuel Certificate
EC	European Commission
RED	Renewable Energy Directive
CEN	Committee for Standardisation
TC	Technical Committee
^{14}C	Radiocarbon
DBFZ	Deutsches Biomasseforschungszentrum
D	Deuterium
IRMS	Isotope Ratio Mass Spectrometry
AMS	Accelerator Mass Spectrometry
pMC	percentage Modern Carbon
VPDB	Vienna Pee Dee Belemnite
SI	The International System of Units
EMPIR	European Metrology Programme for Innovation and Research
TLAS	Tunable Laser Absorption Spectrometer
QCL	Quantum Cascade Laser
VSMOW	Vienna Standard Mean Ocean Water
ISO	International Organisation for Standardisation
TILDAS	Tunable Infrared Laser Direct Absorption Spectroscopy
GPC	Gas Proportional Counting
LSC	Liquid Scintillation Counting
FTIR	Fourier Transform Infrared
CRDS	Cavity Ring-Down Spectroscopy

EXECUTIVE SUMMARY

The biomethane industry is projected to continue growing over the coming decade, and with that growth the technical requirements regarding production and supply are likely to increase. Requirements for biomethane arise from government initiatives and regulations, often though not exclusively associated with the renewable nature of the energy source. The biomethane content of gas grids could potentially be monitored in real-time and or by sampling, at multiple points in the system, whether to demonstrate the origins of the gas stream or to fulfil renewable quota. No United Kingdom or European regulation that requires standardised testing of the biomethane fraction in gas networks currently exists, however the opportunities to implement this method in industry could support future regulations and legitimately quantify the usage of biomethane

This report highlights the potential for future scoping in this area, through the National Physical Laboratory's (NPL's) current capabilities and novel work. Accelerator Mass Spectrometry (AMS), Isotope Ratio Mass Spectrometry (IRMS) and Tunable Laser Absorption Spectrometry (TLAS) were identified as proven methods of measuring biomethane content, albeit of significant infrastructure and practical limitations. AMS and IRMS are unlikely to fulfil the practical requirements of a mobile or accessible biomethane content measurement method, while TLAS would likely require more significant adaption than initially expected to produce accurate and traceable measurements for biomethane. Alternatively, Gas Proportional Counting (GPC), Liquid Scintillation Counting (LSC) and Fourier Transform Infrared spectroscopy (FTIR) were identified as potential techniques, undemonstrated in the context of biomethane and warranting further investigation. All of these techniques will require a more detailed assessment and the development of traceable isotopic gas standards.

It is not evident from this report whether NPL currently has the existing capacity required to develop a practical method for the measurement of biomethane content in gas streams. NPL has a number of relevant capabilities, including but not limited to the development of applicable measurement methods for atmospheric methane, the expertise in biogas and biomethane, and the manufacture of Primary Reference Materials (PRMs). The next steps in the development of this measurement will require a greater understanding of the practical limitations of the techniques discussed in the context of biomethane measurements, and further collaboration with ongoing projects in the contexts of atmospheric methane and isotopic measurements.

1. INTRODUCTION

Biomethane is defined by the British Standards Institution (BSI) as a "*gas comprising principally methane, obtained from either upgrading of biogas or methanation of biosyngas*".[1] Provided the gas meets the relevant requirements, it is then suitable for use as an alternative energy gas to natural gas under the Gas Act.[2,3] In this report, biomethane is distinguished from fossil methane; the former is methane from biogas or more broadly methane generated from biomass by methanogenic archaea, whereas fossil methane is that produced during the thermally-activated breakdown of organic material over an extended period of decay.[4,5,6]

Methane is a significant contributor to climate change and atmospheric chemistry, both as a direct greenhouse gas (GHG) when released fugitively or indirectly through its combustion, which produces carbon dioxide and water, both GHGs, as well as other minor by-products.[4] Biomethane is a renewable alternative to natural gas as it is sourced from biomass. The intake of carbon during biomass growth, the containment of carbon during decomposition and the subsequent reduction in fossil methane usage offsets the GHG produced when biomethane is burnt, with offset variation dependent on biomass type and processing method.[7] It is expected that biomethane and fossil methane will mix; predominantly through the injection of biomethane into the natural gas grid. This consequential blending of biomethane and natural gas supports the requirement for the determination of the biomethane content of a methane stream. This would be needed to quantify the fraction of biomethane, providing evidence of the renewable methane content of a system. At present, there has been only limited investigation into this, which necessitates this review to determine the industrial requirements for measuring the biomethane content within gas grids. This report is part of the National Physical Laboratory (NPL) National Measurement System (NMS) Cross-Theme Project; Enhancing Environmental Monitoring Capabilities for Radiation Safety, Decommissioning and Land Quality. In part, the project aims to investigate the capabilities of NPL to determine the biomethane content of gas streams, and subsequently develop a measurement service in the area to support emerging requirements.

NPL is in direct contact with a global stakeholder network of over 40 companies who have supported its research projects on underpinning biomethane conformity assessment. There is a history of over 10 years of biogas and biomethane research within NPL, that has directly supported growth in the biomethane industry in the United Kingdom (UK) and worldwide. NPL currently offers novel primary reference materials (NPL PRMs) for a selection of biomethane impurities, such as siloxanes. With the development of biomethane content measurement there is potential for NPL to expand its biomethane capabilities. In this report, the current UK and European industrial need for this type of measurement have been reviewed as well as a discussion of the feasibility of the currently available methods to determine the biomethane content of a natural gas stream.

2. UK REQUIREMENTS FOR BIOMETHANE CONTENT MEASUREMENT

According to the Parliamentary Office for Science and Technology (POST), in 2017, UK heating contributed to 20% of UK GHG emissions.[7] From that, 20%, natural gas used for heating was responsible for 14% of the GHG emissions in the UK, making it the single largest contributor in heating to GHG emissions. The distribution of this natural gas through the National Transmission System (NTS), managed by National Grid Plc (NGP), and the subsequent gas distribution networks (GDNs) and independent gas transporters (IGTs) are responsible for the gas supply of around 90% of UK households. Since 2014, biogas upgraded to biomethane has been injected into GDNs by certified installations.[8] In 2018, biomethane contributed to 0.4% of supply and that figure has the potential to increase 10 to 20-fold over the next decade.[7-11] This growth will support the security of the UK's energy system, while improving self-sufficiency through a reduced dependence on imported gas. In the scenario where the UK biomethane industry reaches its full potential and delivers 10% of UK domestic gas demand it would provide heating to 6.4 million homes that would previously have been heated by natural gas. Biomethane can be produced locally, and it not reliant on climate conditions but limited only by the availability of feedstock, which for waste sources is relatively plentiful.[12]

Sources of biomethane include biogas from anaerobic digestion (AD) and bio-synthetic natural gas (BioSNG), of which the latter could theoretically contribute a further 15% of the UK's current gas demand.[7] Currently, biomethane injected into the grid is entirely from AD, as the UK's first commercial BioSNG plant delayed operation from 2018 to 2020.[7,13] Both methods rely upon biomass feedstock, however the composition of their respective biomass differ significantly and can be considered distinct, whereas less distinct sources such as landfill gas may be included under AD. When integrated into gas networks, both sources would be theoretically detectable as renewable content through their measured biomethane fractions by the sampling or online methods discussed in section 4. However, where there are multiple sources of biomethane present knowledge of the origin and composition of the respective biomasses has been suggested to be an essential aspect in minimising the associated uncertainties in measurements once blended with fossil derived streams.[14] According to the National Non-Food Crops Centre (NNFCC), in 2018 there were at least 486 AD plants in the UK, which included 84 biomethane to grid plants, and that a further 343 AD sites were in development.[15] In 2020, 94 biomethane to grid plants inject biomethane into GDNs across the UK, with the NGP Future Energy Scenarios (FES) suggesting biomethane could contribute 46% of total gas supply by 2050.[16,17] The energy networks association (ENA) funded Pathways to Net-Zero report expects AD to grow at a rate of 20 new AD plants every year, increasing to 40 a year from 2029.[18]

In general, the growth in the UK biomethane industry has been driven by a number of Office of Gas and Electricity Markets (Ofgem) led initiatives, often on behalf of the Department for Business, Energy & Industrial Strategy (BEIS). These include but are not limited to; the non-domestic and domestic Renewable Heat Incentive (RHI), Renewable Energy Guarantees Origin (REGO), Feed-in Tariffs (FIT), and Renewables Obligation Certificates (ROCs), of which the latter two ceased in 2019 and 2017, respectively.[19] These environmental programmes offered financial aid and promotion mechanisms to increase the usage of renewable energy sources, and subsequently represent vital incentives for biomethane producers to justify their investment. The REGO scheme exists to provide evidence to end users of the renewable nature of the energy source but appears to focus on installations that generate and export electricity rather than gas to grid operations. Similarly, the FIT scheme encourages renewable electricity generation, however both schemes will still have supported the growth of AD development, albeit in electricity generation. Larger scale renewable electricity projects are supported by ROCs until 2037, 20 years after it closed to new applicants. It is noted that the current requirements of these schemes do not appear to test for the biomethane fraction of the gas generated, however with the predicted growth driven by a supportive policy environment in the biomethane industry the evidence needed to prove renewability may expand.[10]

The RHI supports the use of biogas to heat domestic and non-domestic properties, but is expected to come to an end in 2021, and alongside FIT and ROCs will need to be renewed or replaced by alternative investments to support the continued growth of UK biogas.[16,18] It is important to the UK biomethane industry that over the coming decade a number of new governing schemes will be developed, and it is in these new schemes that the opportunities to employ biomethane fraction measurements are likely to arise. Alongside government structures, independent certification schemes (ICS) such as the Biomethane Certification Scheme (BMCS) and the Green Gas Certification Scheme (GGCS) have existed.[20,21] The BMCS aims to provided certification of the value of biomethane, notably in line with the concept of using biomethane fraction measurements as evidence of renewable content, however the scheme operates similarly to the RHI and does not appear to verify renewability through such a measurement.[20] Similarly, GGCS operate alongside an existing scheme, REGOs and track the contractual flow of biomethane rather than physical flows.[21] Amongst all these programmes there appears to be the requirement for more incentives to upgrade biogas to biomethane, through the decrease of carbon dioxide and carbon monoxide content.[18] At present, approximately 30% of biogas production is upgraded to biomethane, and it is expected that policy will need to change to enable further biomethane injection into the gas networks.

A number of requirements for biomethane exist alongside these initiatives and related regulations, on top of previous requirements for the gas grids. This usually includes compliance with the Gas Act and subsequent legislation, the Renewables and Combined Heat and Power (CHP) register, British Standards

(BS), and the Fuel Mix Disclosure (FMD) as a minimum, often through the Ofgem schemes listed previously.[2,3,19,22,21] BS EN 16723-1:2016 describes the specifications for biomethane injection into the natural gas network, and although notably not all biomethane producers are directly involved with grid injection, there is currently no requirement to conform to this standard or confirm the biomethane fraction of supplied gas.[1] There is a potential for the biomethane content of gas grids to be monitored in real-time or by sampling, at multiple points in the system, whether to prove the origins of the gas stream or to fulfil renewable quota. No UK regulation requiring standardised testing of the biomethane in gas networks has been identified. However, the incorporation of this measurement into GDNs and biomethane producers could prove beneficial to protect against fraud and demonstrate the renewable content of their gas stream.

NGP are currently working on connecting the first biomethane injection point to the NTS by 2020, and while the current status of the project is not evident, NGP reference the UK's Clean Growth Strategy in this decision.[24] The Clean Growth Strategy states that decarbonising the gas grid will require substituting natural gas with biomethane, notably through the RHI.[25] Outside of the NTS, biomethane introduction into GDNs is now relatively commonplace, and NGP, Cadent Gas Ltd, SGN, Northern Gas Networks (NGN), and West and Wales Utilities (WWU) all identify biomethane as an important contributor to a low carbon grid.[26-30] When injecting biomethane into the GDN, a Network Entry Agreement (NEA) is used to define the terms of injection. The NEA is a contract between the GDN and the biomethane generator, and contains acceptance criteria for gas onto their network, including gas quality along with the method(s) for measuring and reporting quality to the GDN. With the importance of fulfilling renewable obligations, it would be possible for future NEAs to require biomethane fraction measurements as proof of the renewable content of their gas stream. Presently, technical requirements and grid capacities do not facilitate biomethane injection, and the suggestion is for these to be made more accessible and standardised.[18] NGN refer to the point of gas injection into the grid as a Biomethane Network Entry Facility (BNEF).[12] The gas analysis for a BNEF, as stated by NGN in 2015, requires online gas chromatography (GC) measurement capabilities, which also includes measurement of the carbon content of methane and carbon dioxide in the output gas. At this stage in the introduction of biomethane into the grid, the measurement of biomethane content could be essential in order to accurately determine the biomethane content of blended gases at other points in the network. Other GDNs offer similar guides to biomethane to grid injection, however none appear to include a reference to proof of source and the other technical requirements vary between GDNs.[18,31]

The development of this relationship between biomethane producers, the GDNs and governing bodies will dictate the technical requirements of biomethane in the future. One such area of development is the current gas safety, metering and billing regulations as set out by the Gas Safety (Management) Regulations 1996 (GS(M)R) and the Gas Calculation of Thermal Energy Regulations (GCOTER).[32,33] The GS(M)R stands as the current UK legislation for regulating the quality of gas injected into GDNs, and dictates the minimum requirements of NEAs. The Institute of Gas Engineers and Managers (IGEM) and ENA are in active discussions regarding the GS(M)R, and IGEM have suggested raising the permitted oxygen content in line with current exemptions to facilitate the injection of biomethane, which is typically higher in oxygen content than natural gas.[17,18] IGEM suggest this change, alongside others to promote low carbon gases would ultimately encourage further growth in the biomethane industry, and they also note the potential of using biomethane in tandem with carbon capture storage (CCS) to provide negative emissions.[16] Developments such as this will undoubtedly expand the technical requirements of the biomethane industry. Another change to regulations will revolve around gas billing methods, as at present, gas billing is based off the flow weighted average calorific value (CV) in each of the 13 local distribution zones (LDZ).[7,32] Given biomethane has a lower CV than natural gas, propane is added (on average 4%) to increase this value resulting in increased operating costs and carbon footprint.[7,18] The Future Billing Methodology (FBM) project aimed to propose updates to the current billing method to negate this, however as it was due to reach completion in March 2020 the current status of the project is not clear.[18,34] Alongside the FBM, SGN's Real-Time Networks (RTN) project for developing live modelling is due to reach conclusion this year, and both projects will certainly affect any opportunity to implement biomethane fraction measurements in this area.[35] Although it is plausible, that a method of determining the content of biomethane and natural gas in a LDZ could also aid to overcoming this issue by distinguishing the lower CV biomethane, it is probable the solution will involve a distinct change to the method of determining CV and energy content.

The capacity for using biogas and biomethane outside of heating is considerable, and although it is not the focus of this report it is important to address the potential for renewable content measurements in other sectors. In the transport sector, biomethane can be used in the form of compressed natural gas (CNG) or liquefied natural gas (LNG) in modified vehicles in the place of petrol and diesel.[10] The whole UK AD industry has sufficient capacity to produce enough biomethane to power 80% of bus fleets or 75% of all heavy goods vehicles (HGVs) in the UK. On top of decarbonising transport fuel, biomethane offers a reduction in cost, nitrogen oxide emissions and particulate emissions. As a result, several commercial biomethane refuelling stations for vehicles are already in operation at UK sites.[10,21] The use of biomethane in transport shares some of the incentives as power but also receives independent schemes, notably the Department for Transport's (DfT) Renewable Transport Fuel Obligation (RTFO).[36] The RTFO is the government's primary programme for renewable transport, including road vehicles, inland water vessels and aircraft to incentivise renewable fuel usage through Renewable Transport Fuel Certificates (RTFCs). Large scale suppliers are obligated to participate, while small scale suppliers can buy in, however RTFCs cannot be used in tandem with RHI or ROCs. The RFTO provides quantitative methods for providing evidence of the renewable content of different fuel categories, such as calculating the fraction sourced from renewable feedstocks based off mass and CV at least every three months. Therefore it is noteworthy, that the RTFO may also accept radiocarbon (^{14}C) dating as evidence of renewable content on a case-by-case basis, and over the next decade as the RTFO and other schemes are introduced and amended, the opportunity to use biomethane fraction measurements as evidence of renewable fuel content may arise. BS EN 16723-2:2017 describes the specifications for biomethane for automotive fuel, and similarly with biomethane for injection does not consider the confirmation of the renewable content of biomethane.[37] Many of the opportunities for implementing this measurement into the transport industry would revolve around provision of evidence of renewable content for regulatory bodies.

The growth of the UK biomethane industry is expected to continue throughout the coming decade, and with it the technical and regulatory requirements, although it is not yet evident what role renewable content measurements will play.

3. EUROPEAN REQUIREMENTS FOR BIOMETHANE CONTENT MEASUREMENT

Many of the requirements laid out in the previous section are reflected in the European biomethane industry, and established UK regulations and incentives are often conceived in Europe, such as the 2015 21st Conference of Parties Paris Agreement, or the European Commission (EC) through the Renewable Energy Directive (RED) and the European Committee for Standardisation (CEN).[38-43] This includes EC issued mandate M/475 to CEN, concerning the specifications for biogas and biomethane for injection into natural gas grids and for use as transport fuel, and subsequently the CEN technical committee (TC) 408 for biomethane that developed the EN 16723 referenced previously.[1,37,44] Mandate M/475 is for the development of ENs for quality specification of biomethane and was issued to facilitate market penetration of biomethane. This is noted to specifically include a method such as ^{14}C isotope analysis or equivalent to determine the volume fraction of biomethane in the pipeline, in order to better manage taxation and fraud.[44,]45

Europe is a world leader in biogas and biomethane production, figure 1 shows European capacity exceeding 10 GW from 17,000 biogas plants in 2015, but since growth rates have appeared to slow.[42,43,46] Many countries around Europe, including Austria, Switzerland and the Nordic countries exhibit a similar usage or growth of biogas to the UK, with support schemes significantly contributing to this, while Germany and Italy stand out from the rest.[42,43,46,47] Germany is the key contributor to biogas technologies in Europe, with 62% of biogas plants in 2015 and as much as 50% of prominent biogas infrastructure manufacturers in Europe.[48,49] The energy supply for electricity and heat generation from biogas more than doubled in Germany in the five years following 2010, with the total number of biogas plants in

Germany now exceeding 10,000 and the number of biomethane plants reaching over 200.[46,50] Europe has shown large uptake of biogas and biomethane industries this decade, but as with the UK the further development of these will require a resurgence in financial incentives and infrastructure accessibility. The *Deutsches Biomasseforschungszentrum* (DBFZ), Leipzig estimate the potential of biogas in the EU to be in the range of 152 to 246 billion Nm^3 from both AD and BioSNG, with the biomethane industry reaching 18 to 20 billion Nm^3 by 2030.[42] As in the UK, Europe's requirement for biomethane measurements is not clear and will depend on the new or improved government support schemes over the next decade, however Germany understandably stands out as the country with the greatest opportunity for implementing biomethane fraction measurements in Europe.

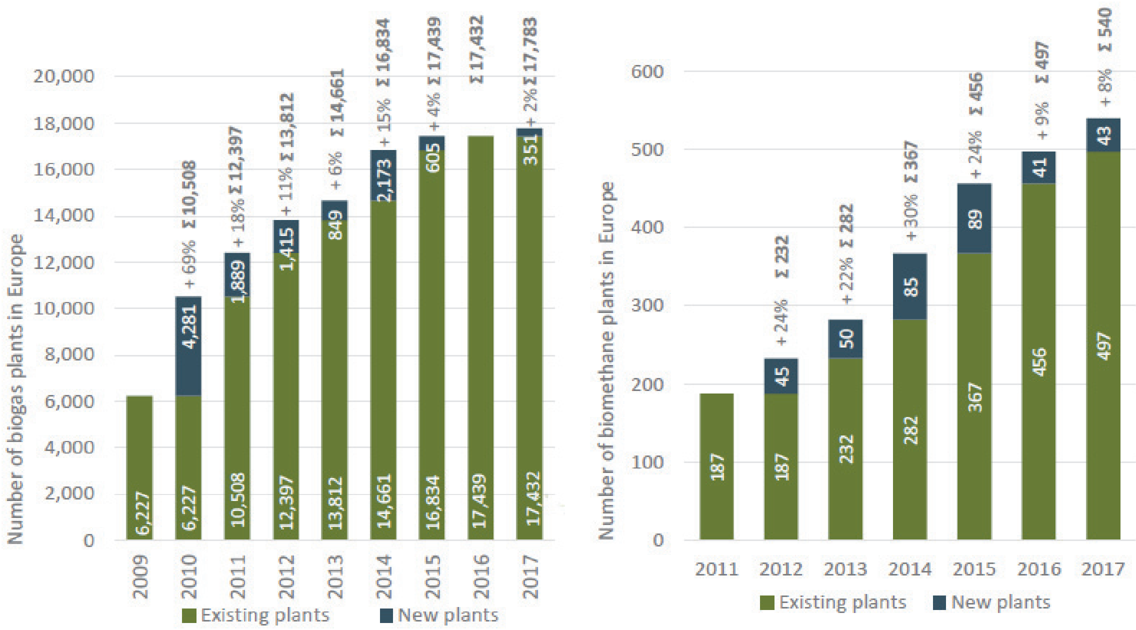

Figure 1: The development of the number of biogas plants (left) and biomethane plants (right) in Europe up to 2017.[46]

The use of biomethane as a transport fuel had its largest global market in Europe in 2015, with almost 700 biomethane filling stations.[42] Many of the factors affecting the growth of this industry in the UK are reflected in Europe, largely because much of UK renewable legislation has been established in Europe; the BS EN 16723-2:2017 was introduced by CEN, and the UK's RTFO cites EC Directives and the RED.[36,37] Currently, biomethane contributes to a relatively small fraction of European transport fuel, predominantly in Germany and the Nordic countries, however shows a high rate of development.[42,50] The implementation of biomethane fraction measurements in UK renewable transport would open the application to the wider European market, and at present there does not appear to be evidence of this measurement in use in the transport industry. From this review, there does appear to be a limited use of methods to measure renewable content within the biomethane industry, and there are a number of methods that do exist in literature, notably several in collaboration with the DBFZ.[51-53] The methods of measuring renewable content will be discussed in greater detail in the next section, however it is noted that the carbon isotopic fractionation, ^{13}C may be used in place of ^{14}C measurements. Lv *et al.*, at the Helmholtz Centre for Environmental Research, Leipzig have used the ^{13}C measurement of biomethane fraction as an indicator of methanogenic pathways and reactor issues in biogas reactors.[51,53] Polag *et al.* at the Institute of Earth Sciences, Heidelberg employed a similar monitoring method of biogas reactors, however notably used an ^{13}C laser spectrographic technique to enable online monitoring.[52]

In some cases, the European biogas and biomethane industries are steps ahead of the UK, with Germany, Italy and France leading the European market, however in all cases there is an expectation that this industry will continue to grow, and with it more technical challenges will arise.[42,46,54] The development of methodologies to accurately measure the renewable content of gas streams could play a role in these technical challenges, and researchers have begun working on this particular development.

4. EXISTING METHODS FOR BIOMETHANE CONTENT MEASUREMENT

In order to measure the biomethane content within a gas network, a method must be capable of distinguishing fossil methane and biomethane in a gas mixture. This is possible through isotpoic composition mesurements, either through ^{14}C content or the stable isotopes of hydrogen and carbon, the former bearing more relevance to this report.[44] Subsequently, existing methods exploit the variation in carbon isotopes ^{12}C, ^{13}C and or ^{14}C, and hydrogen isotopes ^{2}H (D) and ^{1}H. ^{13}C has a relatively high natural abdundance at approximately 1 cmol mol^{-1}, whereas D is scarcer at around 100 µmol mol^{-1}.[55] In constrast, ^{14}C is naturally present at around 1 pmol mol^{-1} amount fractions in modern and living materials suggesting a very challenging measurement without pre-concentration or very selective techniques, however, ^{14}C content is a reliable indicator of a modern source of carbon as it remains unchanged through chemical reactions.[56] It is important to note that atmospheric ^{14}C varies significantly with time as a result of the increased levels from nuclear testing in the 1960s.5[7] Subsequently, feedstocks that have exchanged carbon with the environment for a significant period of time such as wood waste can show increased amounts of ^{14}C.[58]

Fossil sources of methane do not contain ^{14}C, due to the 5730 year half life they have become depleted from extensive decay over hundreds of thousands to millions of years after formation.[56] As a result, by measuring the ^{14}C content of blended biomethane and fossil methane it is possible to determine the fraction of biomethane in a gas stream.[59] Due to the absence of ^{14}C in fossil methane, there is theoretically a linear relationship between the biomethane fraction and the measured ^{14}C fraction. In part, the establishment of this method came from work by Palstra and Meijer, which drew upon learnings in the measurement of the ^{14}C fraction of carbon dioxide emissions in flue gas.[14] Palstra and Meijer combusted their sampled biogas, intially measured the ^{13}C value of the resulting carbon dioxide using isotope ratio mass spectrometry (IRMS) and then once graphitized, determined the ^{14}C value by accelerator mass spectrometry (AMS). The method required a significant number of treatments between sampling and measurements, but notably the pretreatment of the biogas samples in this study was similar to that required to obtain biomethane. The value of $^{14}C_{sample}$ is calculated as the percentage modern carbon (pMC). The pMC value is corrected for isotope fractionation and for decay of the calibration material, an oxalic acid standard with a known value of ^{13}C relative to the Viena Pee Dee Belemnite (VPDB) scale. The VPDB is an internationally agreed reference scale for ^{13}C and ^{13}C measurements must be normalised to the VDPB scale using at least two suitable international reference materials.[60,61] The VPDB was originally based off the PDB calcite source which was exhuasted, more recently the NBS 19 limestone source and LSVEC lithium carbonate source, both of which are limited resources resulting in a further 30 reference materials and consequetial tracability issues. Additionally, absorbed carbon dioxide in these reference materials results in drifting isotope ratios and systemic errors in the use of acids to liberate this into the gas phase.[60,62] The development of methane reference materials traceable to the International System of Units (SI) is part of the European Metrology Programme for Innovation and Research (EMPIR) project for stable isotope metrology to enable climate action and regulation, comencing in 2020 and coordinated by NPL.[63] Furthermore, Palstra has been involved with the development of methods for determing the isotopic composition of biomethane, to support CEN TC 408 and this work is due to be published in Summer 2020.[44]

Kääriäinen *et al.* adopted a different approach to overcome the lack of online in-situ analysis presented by Palstra and Meijer.[14,59] An alternative tool to ^{14}C measurements is offered; analysis of the stable isotopes ^{13}C, ^{12}C, D and ^{1}H, and specificically the ratio of the respective pairs (^{13}C and D) in a sample arising from the presence of methane isotopologues $^{12}CH_4$, $^{13}CH_4$, and CH_3D. Kääriäinen *et al.* employed optical detection using a tunable laser absorption spectrometer (TLAS) to permit real time measurements. Kääriäinen *et al.* cite previously existing optical methods for studying stable methane isotopologues, notably Mid-IR absorption and quantum cascade lasers (QCL), however not in biomethane and natural gas mixtures. As with Palstra and Meijer, the isotopic ratios are defined relative to the VPDB for ^{13}C, however the Vienna Standard Mean Ocean Water (VSMOW) scale was used for

D. The VSMOW suffers similar drift and tracability issues to the VDPB due to the limited nature of the reference material, and along with the Standard Light Antartic Precipitation (SLAP) standard the orignial reference materials have already been exhausted and replaced.[64] It is noteworthy, that to validate the TLAS, mixtures of natural gas and biomethane were volumetrically prepared at 10 bar in stainless steel vessels, to an uncertainty of 0.1% according to the International Organisation for Standardisation (ISO) 6144.[65] These 'reference gases' were then run through the TLAS against the sample gases using a switching method, to produce an uncertainty in the biomethane fraction comparable to the work of Palstra and Meijer.[14,59] It is noted that both ^{13}C and D measurements are required to accurately distinguish sources of methane as graphically represented in figure 2, taken from Sherwood *et al.*[66]

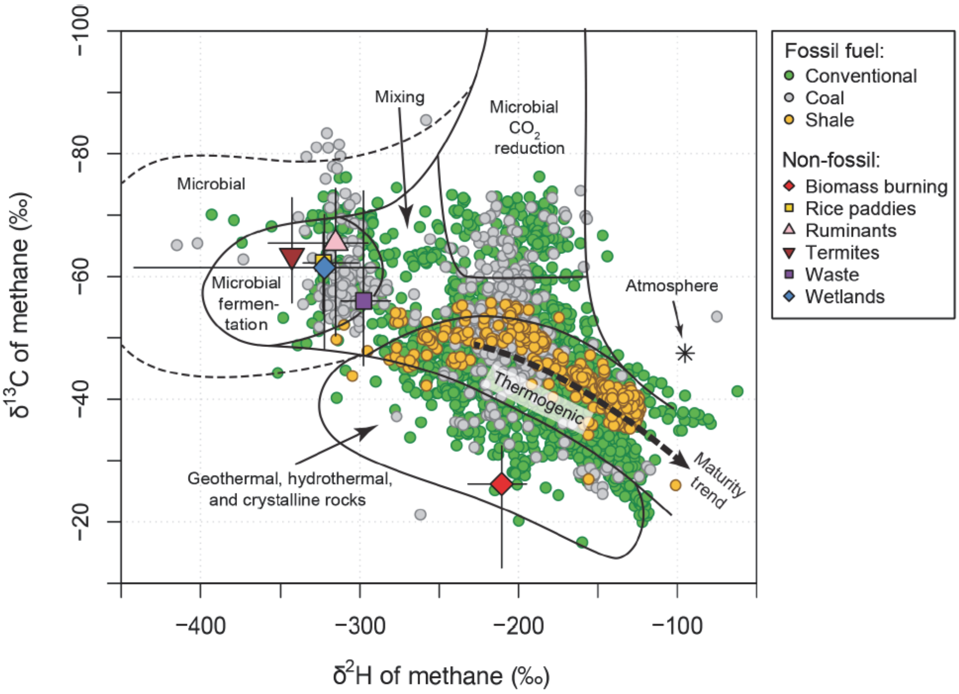

Figure 2 - Genetic characterization plot of $\delta^{13}C$ methane versus δD methane showing data distributions with respect to genetic domains.[66]

Both Kääriäinen *et al.*, and Palstra and Meijer cite European Commission Directives as motivation for developing their methodologies.[14,40,41,59] Both studies suggested that knowledge of the isotopic composition of the source material is necessary to reduce the uncertainty in determining the biomethane content, however methods using ^{14}C, ^{13}C and D afford the direct and independent distinguishing of biomethane from fossil methane fractions.[14,56,59] This uncertainty may arise in decay corrections for the sample measured and respective calibration standard, and in the case of gas mixtures where the biomethane source is not separately available the source biomethane fraction needs to be approximated based on atmospheric carbon dioxide isotopologue, $^{14}CO_2$ data and time origin. Further studies have used IRMS to distinguish biomethane from fossil methane, and also highlight issues regarding the intergration of biomethane into fossil sources prior to extraction.[5,67]

In contrast to methane fuel systems, the differentiation of biomethane and fossil methane sources in atmospheric methane is more widespread, however this requires a method to measure methane concentrations at ambient levels or the preconcentration of methane to high amount fractions without causing isotopic fractionation. This is potentially a higher complexity than if applied to high concentration methane fuel samples, although these are not without their possible issues including flammability and explosion hazards and detector saturation. Atmospheric studies appear to exhibit a similar span of methods to those used with fuel systems, with carbon and hydrogen isotope ratios implemented and IRMS employed for isotopic measurements, however with a larger focus on sampling methods and simulation modelling due to the atmospheric context.[68,69] IRMS has also been applied to glacier meltwater as a source of biomethane, and there are potential learnings to be taken from both these areas for method development in fuel systems.[70]

NPL currently has a range of capabilities that overlap with the methods and requirements described in this report, however it is notable that NPL does not currently have capabilities in AMS or IRMS. At present, NPL uses tunable infrared laser direct absorption spectroscopy (TILDAS) to measure the amount of methane isotopologues $^{12}CH_4$, $^{13}CH_4$ and $^{12}CH_3D$ in a sample as compared to gas standards, by a switching method as shown in figure 3. From the measured ratio of isotopologue amount fraction the isotope ratios ^{13}C and D may be calculated to a level of precision close to that attainable by mass spectrometry. At present, this method is employed for measurements of atmospheric methane, after prec-concentation to around 500 µmol mol^{-1} in nitrogen and is capable of resolving changes in ^{13}C and D to apportion methane between its different sources, specifically to demonstrate compliance with international agreements for decreases in fossil methane. Previous work using TILDAS on higher methane concentrations, observed clumped isotopologues through a methane isotope geo-thermometry method.[71]

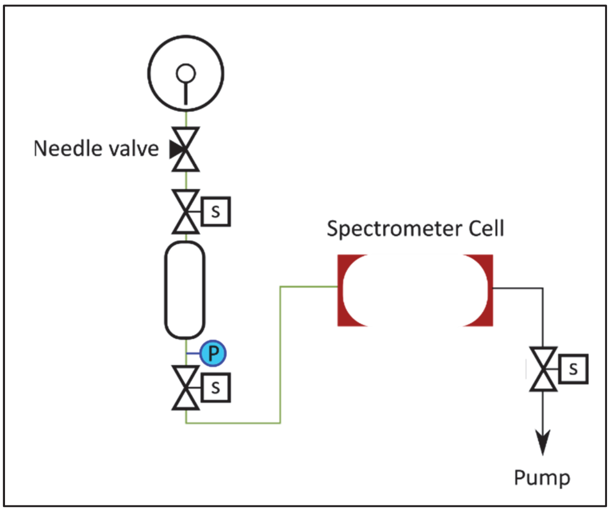

Figure 3: The simplified schematic for NPL's TILDAS system's, showing the selector valve for switching between the sample and standards, additonal valves for adjusting the flow of gas.

Calibration is dependent on the standards bracketing the methane amount fraction of the sample, and subsequently a knowledge of the sample's isotopic composition is required. Pure methane samples can be diluted to within the brackting standards, or a reliable source for high-purity biomethane used to produce bracketing standards. Currently, it appears the variation in the isotopic composition of manufactured methane raises a significant difficulty in developing methane standards, and the verification of these compositions through dilution and established isotopic techniques adds further practical limitations to the application of this method in the context of biomethane. Additionally, the use of high methane amount fractions would require suitable safety considerations aligned with the increased flammability and explosive risk. Were these issues to be overcome, NPL can produce such standards as PRMs *via* gravimetric methods for this service, according to ISO 17034 and ISO 17025 and superior to the volumetric standards used by Kääriäinen *et al*.[14,72,73]

AMS, IRMS and TLAS appear the primary instruments of biomethane fraction measurements in literature and would be theoretically favourable methods for the development of biomethane content measurements, however their expense is a significant drawback and more financially practical methods warrant investigation. As a result of this review, further scoping is required into the feasibility of alternative methods, notably methods involving ^{14}C for the benefits highlighted previously such as gas proportional counting (GPC) and liquid scintillation counting (LSC).[56] These radiometric methods differ from spectrometric analyses, in that the measurement of isotopic compositions comes from measuring the -particle radiation from the decay of ^{14}C.[74] These technique encounter issues from the relatively low radioactivity of ^{14}C and energy of the emitted -particles, however modern radiometers have resolved a number of these. Notably, LSC offers a low cost per measurement, has been used to successfully determine the ^{14}C content of bioethanol and biodiesel and GC may also be used in tandem as GC-LSC to analyse $^{14}CH_4$.[58,75,76] No GPC or LSC methods for measuring biogas or biomethane have been identified by this report, however typically samples are converted into the gas phase as carbon dioxide and the use of methane as a counting gas in GPC warrants further investigation into both techniques. GPC and LSC are current capabilities in the Nuclear Metrology Group at NPL. There is also the consideration of alternative spectroscopic techniques that have not been identified in biomethane studies. Fourier Transform Infrared (FTIR) spectroscopy has been used to determine ^{13}C in a number of atmospheric studies of carbon dioxide and methane.77,[78] Although this report has not identified an isotope study of biomethane using FTIR, the technique has been used to characterise biogas with NPL resulting in the opportunity to avoid initial practical limitations.[79,80]Another relevant spectroscopic technique undemonstrated in the measurement of biomethane fuel is the development of Cavity Ring-Down Spectroscopy (CRDS) methods for ^{14}C measurements.[81,82]

This report has highlighted some potential future work and opportunities in this area initially as part of the ongoing NPL NMS Cross-theme Project and the GPMG as a whole. Firstly, further investigation into a method of biomethane content measurement will require the use of existing NPL capabilities, for example favouring techniques such as GC-LSC over AMS and FTIR over TLAS. These techniques will require a more detailed assessment, beyond the limited acknowledgement in this report. Secondly, the capability to support such a measurement will require investigation, such as the laboratory sampling or generation of biomethane, the development of ^{14}C reference gases and the conversion of methane into $^{14}CO_2$, the latter two of which will be under investigation in ongoing and future atmospheric projects at NPL.

5. CONCLUSIONS

It is evident that the biomethane industry is expected to continue growing into the coming decade and beyond, and that as it expands the technical and legislative requirements will need to expand as well. Although it is not yet clear what role measurements regarding the biomethane fraction of gas streams will play, there is certainly the potential for its employment in the industry. It has been highlighted that knowledge of the isotopic composition of a biomethane source is important when distinguishing biomethane and fossil methane. Subsequently, the opportunities to implement biomethane content measurements would likely involve the measurement of isotopic composition at the stage of biomethane production to afford accurate measurements elsewhere in the gas network.

It is not evident whether NPL has the capabilities to develop a practical measurement method for the biomethane content of natural gas streams, however it does possess a handful of the necessary tools and expertise required. At present the use of NPL's TILDAS is the most promising method to apply to this context, however in the short term this method is inaccessible to development in the area of biomethane content measurements and raises unresolved practical limitations. The use of certain radiometric and spectroscopic techniques has not been demonstrated in the context of biomethane, and subsequently offer an alternative opportunity to realise this measurement in line with current NPL capabilities. NPL is not in a position to develop a feasible method of measuring biomethane content that could be suitably applicable to the industry without further investigation into the practical analytical techniques that fulfil the current lack of demand for this measurement. The next steps for this aspect of the NPL NMS Cross-Theme Project, and the development of this method as a whole will require a greater understanding of the practical limitations of the discussed techniques in the context of biomethane measurements.

In the scenario where new methods or instruments are developed, NPL has the capabilities to collaborate with method development, calibration approaches and the preparation of PRMs. Any new methods could then undergo validation at NPL prior to their adoption, in order for the GDNs and biomethane industry to understand the associated detection limits, and any uncertainties in the measured value. A standard test method for biomethane content would support future legislation and support schemes, and supplement any future NEAs to support the GDNs, biomethane industry and end users in businesses and the home.

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