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127070 DECARBONISING HEAT IN THE UK: PREPARATION PLANS FOR A GAS REFERENCE MATERIAL SUITE ALIGNED WITH STAKEHOLDER NEEDS BASED ON 2021-22 FEASIBILITY REPORT

JOHN ALLDEN

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National Physical Laboratory

Hampton Road, Teddington, Middlesex, TW11 0LW

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Approved on behalf of NPL by
Arul Murugan, Science Area Leader, Gas Metrology Group.

CONTENTS

1 INTRODUCTION

The National Physical Laboratory's (NPL) Gas Metrology Group works with several research areas and measurements to support the energy gas industry including but not limited to natural gas, refinery gas, LPG, hydrogen, biogas and biomethane. NPL's services include investigating and addressing measurement challenges during the production and usage of energy gases, with the view of supporting smooth energy transitions.

NPL also provides primary reference materials (PRMs; gas standards traceable to the kilogram), quality assurance for energy gases, and support for industry with instrument validations, consultancy, and gas purity. This puts NPL in a position to develop PRMs for the emerging hydrogen enriched natural gas, biomethane and hydrogen for heat sectors.

2 SCOPE

This report presents the development of preparation plans for a PRM suite aligned with stakeholder needs based on the 2021-22 feasibility report. Stakeholders may include but are not limited to Gas Network Operators (GNOs), gas producers and equipment manufacturers. Plans will comprise of excel spreadsheets and calculations performed in NPL's inhouse "GravCalc" software to confirm the mixtures are technically feasible to provide to industry.

The PRM suite would expand NPL's capability to support hydrogen enriched natural gas (up to 30% H2 at < 1 % uncertainty), biomethane (trace multi-component EN 16723[i] impurities such as amines, halogenates, water, dust and compressor oil at 1 – 20 % uncertainty) and hydrogen for heat to support UK gas industry (BSI PAS 4444[ii] at 1 – 10 % uncertainty).

3 GAS MIXTURE REQUIREMENTS

The EN16723 and the BSI PAS 4444 specify trace component impurities for biomethane and hydrogen for heat, respectively as shown in Table 1. The existing UK natural gas regulations such as the GS(M)R 1996[iii] will also influence the compositions.

Table 1 – Trace impurities for the EN16723, BSI PAS 4444 and GS(M)R 1996.

Components	EN16723 (Biomethane)	BSI PAS 4444 (Hydrogen for Heat)	GS(M)R 1996 (Natural Gas)
Hydrogen	-	98 cmol mol^{-1}	≤ 0.1 cmol mol^{-1}
Carbon monoxide	0.1 cmol mol^{-1}	20 µmol mol^{-1}	-
Hydrogen sulphide	-	≤ 3.5 µmol mol^{-1}	≤ 5 mg m^{-3}
Total Sulphur	-	≤ 35 µmol mol^{-1}	≤ 50 mg m^{-3}
Total Silicon	0.3-1 mg Si m^{-3}	-	
Oxygen	-	≤ 0.2 cmol mol^{-1}	≤ 0.2 cmol mol^{-1}
Methane	-	≤ 1 cmol mol^{-1}	-
Carbon Dioxide	-		-
Total hydrocarbons	-		-
Water (dew point)	-	- 10 °C	-
Argon	-	≤ 2 cmol mol^{-1}	-
Nitrogen	-		-
Helium	-		-
Ammonia	10 mg m^{-3}	-	-
Amine	10 mg m^{-3}	-	-
Halogenated	1-63 mg m^{-3}*	-	-
Other Impurities	The biomethane shall be free from impurities other than "de minimis" levels of compressor oil and dust impurities. In the context of this European Standard, "de minimis" means an amount that does not render the biomethane unacceptable for conveyance and use in end user applications.	Shall not contain solid, liquid, or gaseous material that might interfere with the integrity or operation of pipes or any gas appliance, within the meaning of regulation 2(1) of the Gas Safety (Installation and Use) Regulations 1998, that a consumer could reasonably be expected to operate.	Shall not contain solid or liquid material which may interfere with the integrity or operation of pipes or any gas appliance (within the meaning of regulation 2(1) of the 1994 Regulations) which a consumer could reasonably be expected to operate.

*EN16723 refers to the CEN/TR 17238:2018[iv] for halogenated components.

The compositions in Table 2, Table 3 and Table 4 for hydrogen enriched natural gas, biomethane and hydrogen for heat respectively are based on feasibility calculations carried out to assess the dew point and maximum pressures obtainable. The amount fractions of the major components in the following compositions are based on current NPL capabilities and services, or directly taken from the standards in Table 1.

4 HYDROGEN ENRICHED NATURAL GAS

GS(M)R 1996 is under review for adjustment to account for increased hydrogen amount fractions while maintaining other amount fractions. Odorant blends in the UK are typically a mixture of tertiarybutyl mercaptan (2-methylpropane-2-thiol, t-BuSH) and 20% dimethyl sulphide (DMS).[v,vi,vii]

Table 2 – Proposed approximate compositions and compositional ranges for hydrogen enriched natural gas with <1% target uncertainties.

Components	Amount fraction / cmol mol^{-1}						
	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6 (1 alt)	Mix 7 (2 alt)
Nitrogen	17.0	10.0	0.40	2.30	0.040	17.0	10.0
Methane	74.26	82.79	54.66	61.99	79.78	51.63	57.86
Carbon dioxide	0.70	0.10	12.50	7.50	0.0550	0.70	0.10
Ethane	3.0	0.30	15.50	6.50	0.050	3.0	0.30
Propane	1.50	0.350	6.0	3.40	0.050	1.50	0.350
iso-Butane	0.0450	0.20	0.350	1.40	0.0060	0.0450	0.20
n-Butane	0.0150	0.070	0.350	0.70	0.0060	0.0150	0.070
neo-Pentane	0.010	0.080	0.150	0.350	0.0010	0.010	0.080
iso-Pentane	0.450	0.220	0.0220	0.060	0.00250	0.450	0.220
n-Pentane	0.40	0.220	0.010	0.0550	0.0040	0.40	0.220
n-hexane	0.050	0.40	0.0120	0.250	0.0010	0.050	0.40
Hydrogen	2.50	5.0	10.0	15.0	20.0	25.0	30.0
Oxygen	0.20	0.20	0.20	0.20	-	0.20	0.20
Hydrogen sulphide	0.000350	0.000350	0.000350	0.000350	0.000350	0.000350	0.000350
DMS/t-BuSH	0.003340	0.003340	0.003340	0.003340	0.003340	0.003340	0.003340

5 BIOMETHANE

GS(M)R 1996 and case-by-case Network Entry Agreements (NEAs) dictate the specifications for biomethane injection into the UK gas network. EN16723 specifies trace multi-component impurities for biomethane, propane at approximately 6% may be added to biomethane to increase caloric value and for the following compositions the halogenated compounds have been simplified to dichloromethane based on current NPL capabilities.[iv,viii] Low and high amount fraction compositions have been proposed in Table 3 – Proposed approximate compositions and compositional ranges for biomethane with 1-20% target uncertainties.Table 3.

Table 3 – Proposed approximate compositions and compositional ranges for biomethane with 1-20% target uncertainties.

Components	Amount fraction / cmol mol^{-1}		
	Mix 1	Mix 2	Mix 3
Methane	-	0.0020	5.0000*
Carbon Dioxide	99.86	99.85	83.25
Nitrogen	-	0.0020	3.2500*
L2 Siloxane	0.0084	0.0084	0.1263
L3 Siloxane	0.0056	0.0056	0.0842
D3 Siloxane	0.0056	0.0056	0.0842
D4 Siloxane	0.0042	0.0042	0.0631
D5 Siloxane	0.0034	0.0034	0.0505

Ammonia	-	0.0014	0.0014
Ethanolamine	-	0.00039	0.00039
Carbon Monoxide	-	0.002	0.1
Dichloromethane	-	0.000110	0.000110
Propane	-	-	6.0
n-hexane**	0.1123	0.1123	1.6838
Hydrogen	-	0.002	0.1
Oxygen	-	0.002	0.2
Hydrogen sulphide	0.00035	0.00035	0.00035
DMS/t-BuSH	0.00334	0.00334	0.00334

*The amount fractions of these components are based on NPL oxy-flam safety requirements – to avoid creating any oxy-flammable mixture oxygen is added with either 2% oxygen in nitrogen or 3% oxygen in carbon dioxide premixtures.

***n*-hexane is included in the mixture to dissolve D3 siloxane in its solid form.

6 HYDROGEN FOR HEAT

GS(M)R 1996 will dictate the initial specifications for hydrogen for heat into the UK gas network. BSI PAS 4444 specifies trace multi-component impurities for hydrogen for heat and low to high amount fraction compositions have been proposed in Table 4. All the components are covered under existing NPL capability albeit in different compositions. In that respect, there is existing stability data for several of these components in hydrogen, however stability data in combination with the other components is still to be collected.

Table 4 – Proposed approximate compositions and compositional ranges for hydrogen for heat with 1-10% target uncertainties.

Components	Amount fraction / cmol mol^{-1}				
	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
Hydrogen	99.999	99.99	98.0	97.0	89.0
Carbon Dioxide	-	0.002	0.50	0.50	3.250*
Nitrogen	-	0.002	0.330	0.660	5.0*
Methane	-	0.002	0.50	0.50	1.0
Helium	-	0.002	0.330	0.660	0.660
Argon	-	0.002	0.330	0.660	0.660
Carbon Monoxide	-	0.002	0.002	0.0020	0.0020
Water	-	0.002	0.020**	0.020**	0.020**
Oxygen	-	-	-	0.024	0.20
Hydrogen sulphide	0.000350	0.000350	0.000350	0.000350	0.000350
DMS/t-BuSH	0.003340	0.003340	0.003340	0.003340	0.003340

*The amount fractions of these components are based on NPL oxy-flam safety requirements – to avoid creating any oxy-flammable mixture oxygen is added with either 2% oxygen in nitrogen or 3% oxygen in carbon dioxide premixtures.

**Water amount fraction is based on a feasible amount fraction in a hydrogen mixture without condensation.

7 CONCLUSIONS AND FUTURE WORK

This report finds that it is technically feasible to provide PRMs for hydrogen enriched natural gas, biomethane and hydrogen for heat. There are still aspects of preparation that require additional assessments, including but not limited to stability data, preparation hierarchies and the analytical techniques for validation, however these developments of NPL's capabilities are well within feasibility.

The requirements for hydrogen enriched natural gas PRMs can be considered covered by NPL's current capabilities, except for the confirmed stability of natural gas components in the presence of high hydrogen content. The key capabilities that will require development are the minor components in both biomethane and hydrogen for heat PRMs, especially when present together in a multi-component mixture.

This future work will require the preparation, validation and stability testing of several of these standards to confirm the practicality of preparing these PRMs for industry stakeholders. In particular, the stability of ammonia, amines, and halogenated compounds in biomethane and the stability of the total hydrogen for heat composition require assessment.

This latter is expected to be covered in part by the EMPIR Metrology for Decarbonising the Gas Grid project, which involves the development of hydrogen for heat PRMs for a 24-month stability study. The missing components from these PRMs which would require further evaluation under NMS are water, and DMS and t-BuSH, as these have been excluded or replaced by tetrahydrothiophene (THT) respectively.

The assessment of some minor components in biomethane including ammonia will be captured by the 21NRM04 BiometCAP project commencing this year, however an assessment of the complete composition of biomethane and any additional components would require NMS funding.

This report has focused on PRM preparation feasibility only, with future reporting next year to cover analytical methods and additional stakeholder input, however this report does suggest there is significant work required for mixture preparation, method development and stability assessment to cover NPL's missing capabilities, particularly for biomethane.

8 REFERENCES

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[ii] BSI, PAS 4444:2020+A1:2021. *Hydrogen-fired gas appliances*.
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[vi] IGEM/SR/16 Edition 2 Communication 1734, *Odorant systems for gas transmission and distribution.*
[vii] BSI, BS EN ISO 13734:2013. *Natural gas — Organic components used as odorants — Requirements and test methods*.
[viii]CNG Services, *Biomethane Enters the Gas Grid*, Article for Energy World