EffecTech

Calibration of Sensor Technology Using Traceable LNG Reference Mixtures

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LNG3 Workshop, Aberdeen

Dr Joey Walker

EngD - EffecTech/Loughborough University – Validation of spectroscopic instruments for the direct measurement of multi-component cryogenic liquid hydrocarbons

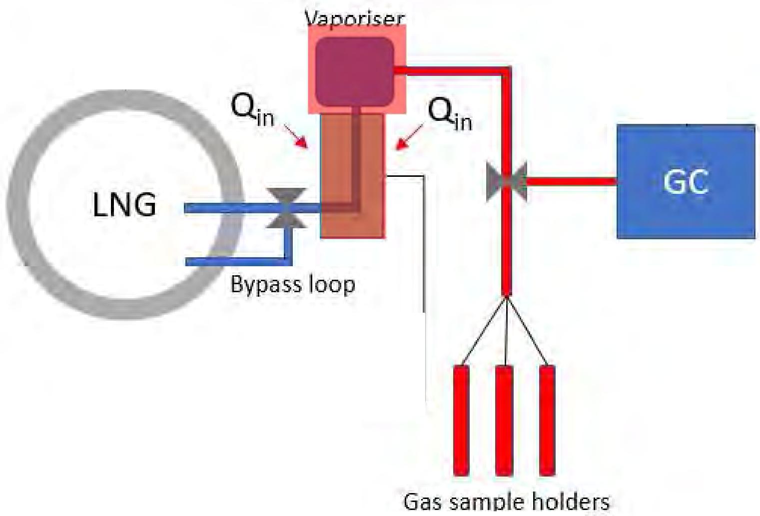
LNG research project started in 2013 at EffecTech labs

Currently employed by EffecTech Ltd
Technical Support Engineer

What prompted the development of direct LNG measurement?

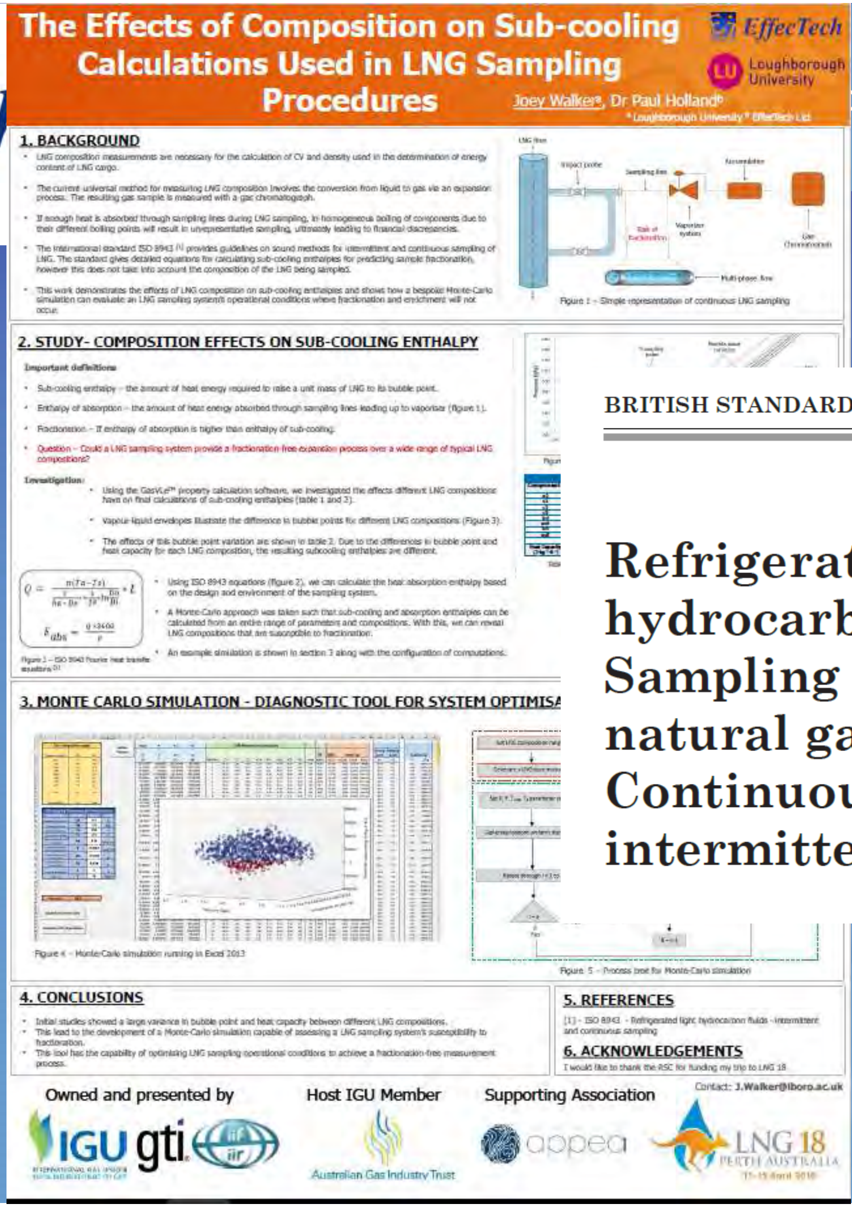
Sampling concerns
Vaporiser concerns

Faster measurement
More accurate
Dynamic process control


Vaporiser
Q_{in}
Q_{in}
LNG
GC
Bypass loop
Gas sample holders

EffecTech

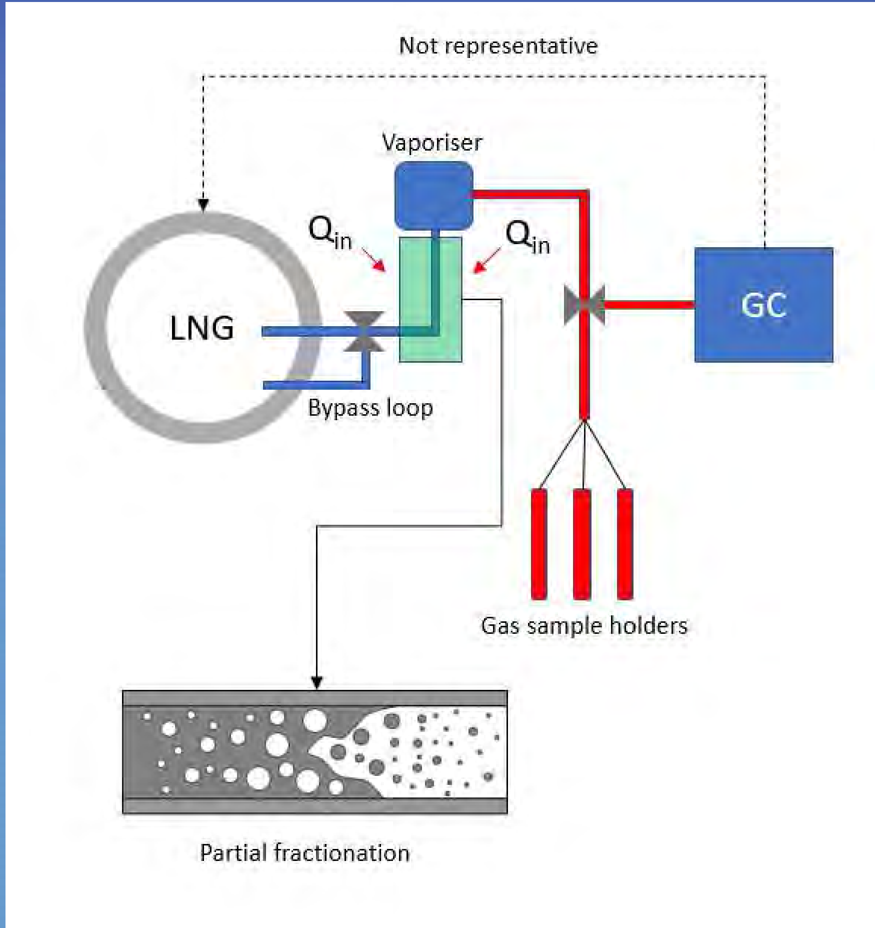
ders in Gas Measurement

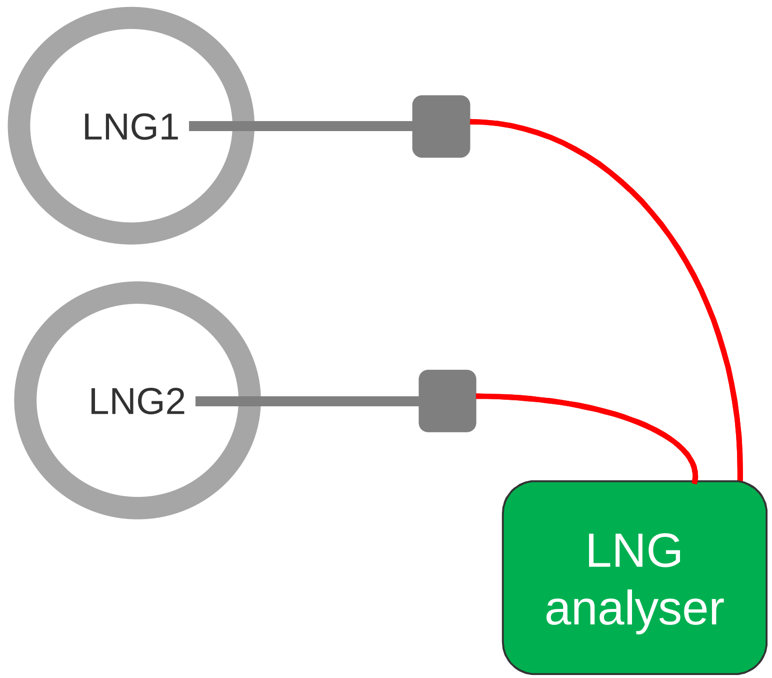


BRITISH STANDARD

BS ISO 8943:2007

Refrigerated light hydrocarbon fluids — Sampling of liquefied natural gas — Continuous and intermittent methods


Not representative
Vaporiser
Q in
Q in
LNG
GC
Bypass loop
Gas sample holders
Partial fractionation


LNG1
LNG2
LNG
analyser

How do we calibrate LNG analyzers?

gas?
cyclohexane standard?

Calibration standard and medium should be the same as what is being measured!

Production of LNG reference standards

Optimal system:

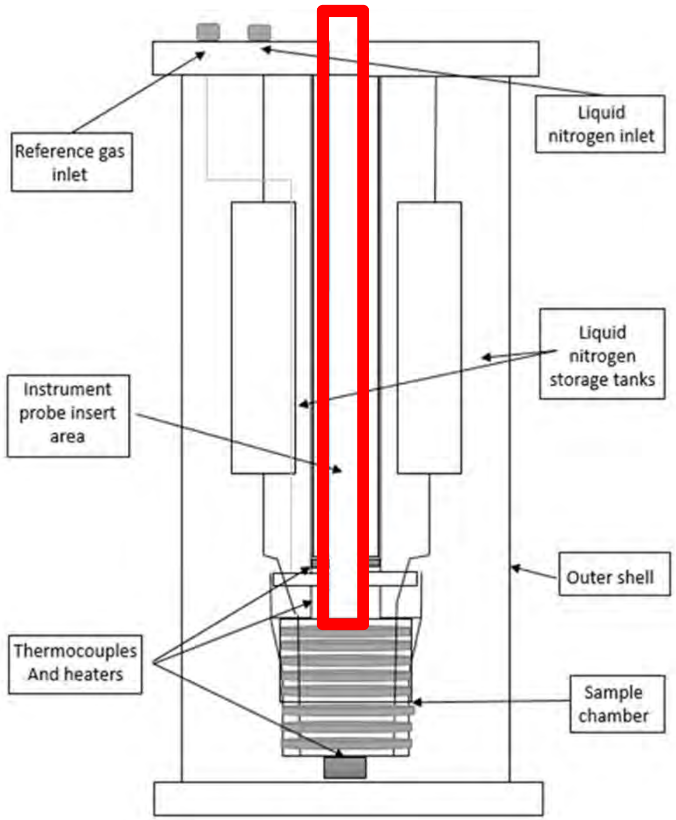
1) efficient gas to liquid conversion
2) temperature control and stability
3) space for a LNG probe
4) ability to sample and measure LNG directly for verification
5) minimal headspace

Initial questions:

How much gas to condense?
What temperature to condense/measure?
Sampling method?
Cooling medium?
LNG range?
Lower/upper limits?
How to evaluate such a system?

Cryostat at EffecTech

- Liquid nitrogen as cooling medium. 7 litre storage tank.
- 3 bar maximum working pressure
- Stainless steel/ copper cell construction
- Space for different probes (50mm diameter max).



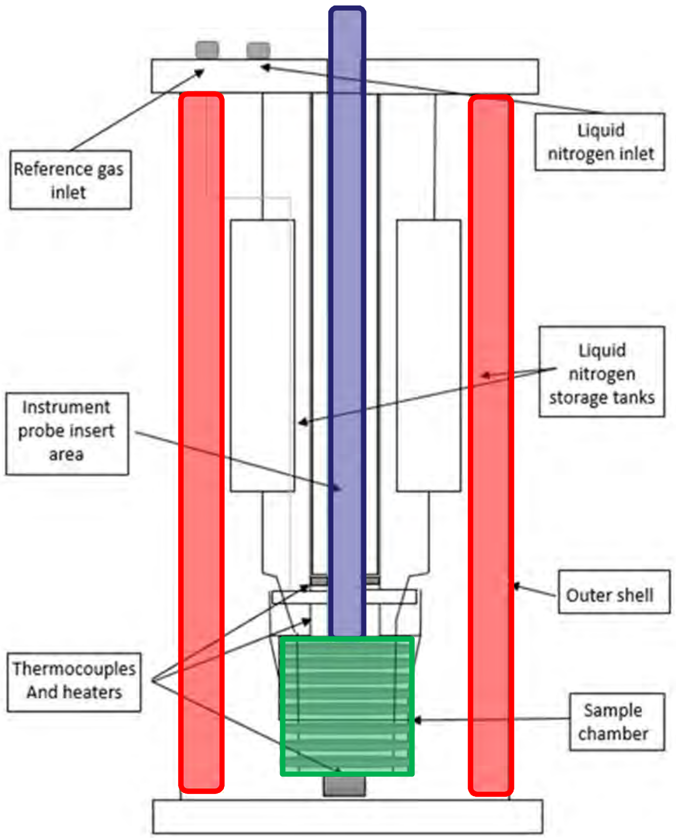
1. Preparation

1. Insert measurement probe

2. Evacuate outer chamber

3. Evacuate sample chamber

10^{-6} mbar

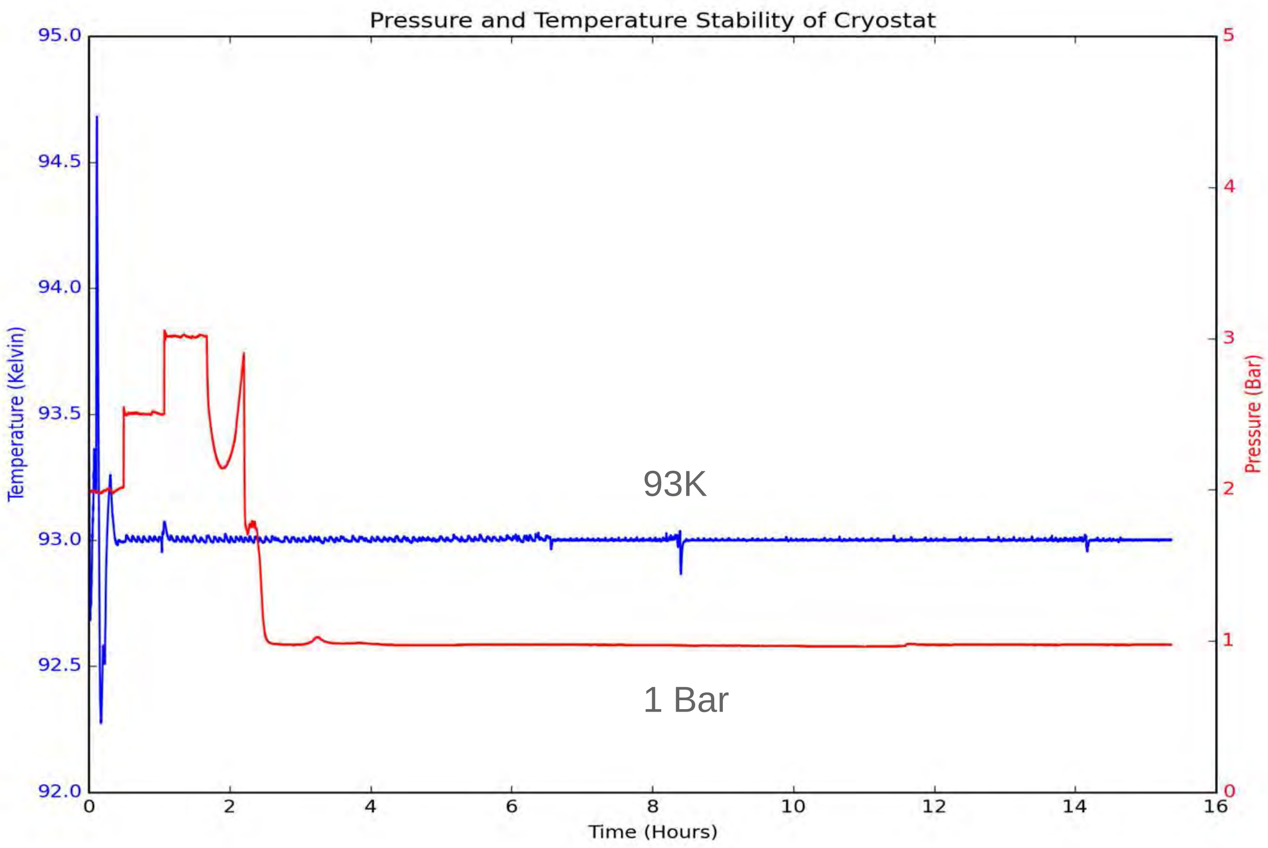


2. Condensati

1. Initial cool-down using liquid N_2

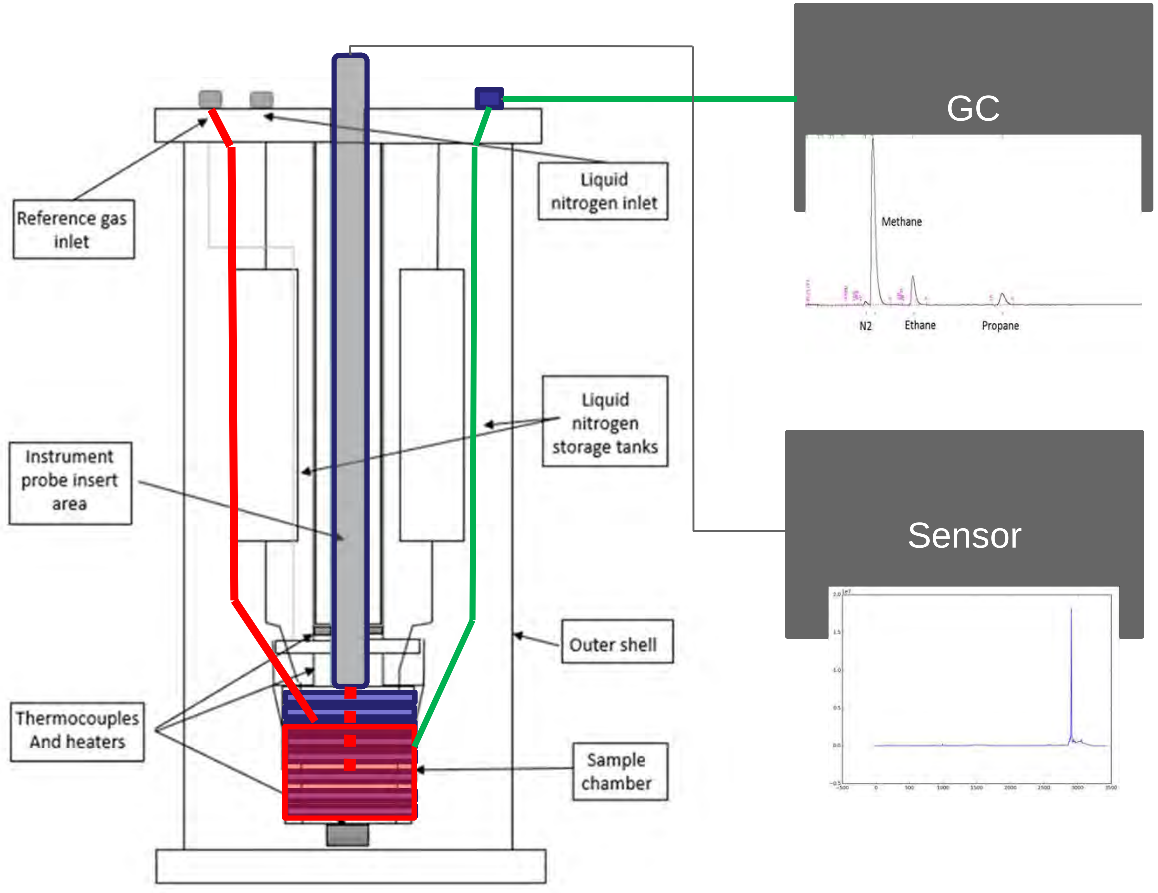
2. Addition of PRGM

3. Thermal control



3. Measurement

1. Connect sample lines to Gas chromatograph
2. Pressurise the system with helium
3. Open outlet and measure with GC and sensor instantaneously




PT 80DRY

Thermophysical predictions

What temperature to condense at?

	Amount fraction (%mol/mol)			
component	**MIX 1**	**MIX 2**	**MIX 3**	**MIX 4**
nitrogen	0.6001	0.1494	1.1657	0.04096
methane	93.0700	98.4376	92.6334	86.848
ethane	5.4810	0.09604	2.7762	10.649
propane	0.6791	0.09362	3.0278	2.0024
iso-butane	0.0597	0.6269	0.13067	0.2059
n-butane	0.0800	0.4297	0.0694	0.24349
iso-pentane	0.0201	0.08232	0.09861	0.004691
n-pentane	0.0101	0.08418	0.0985	0.005378

Boiling point

	Pressure (bar)			
MIX 1	**1**	**1.5**	**2**	**2.5**
Temperature (LRS, K)	110.31	115.65	119.75	123.13
Temperature (RKS, K)	110.65	116.00	120.11	123.49
Temperature (GERG, K)	110.17	115.62	119.81	123.25
MIX 2				
Temperature (LRS, K)	111.22	116.34	120.29	123.54
Temperature (RKS, K)	111.56	116.69	120.65	123.91
Temperature (GERG, K)	111.18	116.40	120.42	123.73
MIX 3				
Temperature (LRS, K)	108.43	113.93	118.14	121.60
Temperature (RKS, K)	108.76	114.28	118.49	121.95
Temperature (GERG, K)	108.16	113.80	118.10	121.63
MIX 4				
Temperature (LRS, K)	112.90	118.15	122.21	125.56
Temperature (RKS, K)	113.27	118.53	122.60	125.96
Temperature (GERG, K)	112.86	118.22	122.35	125.77

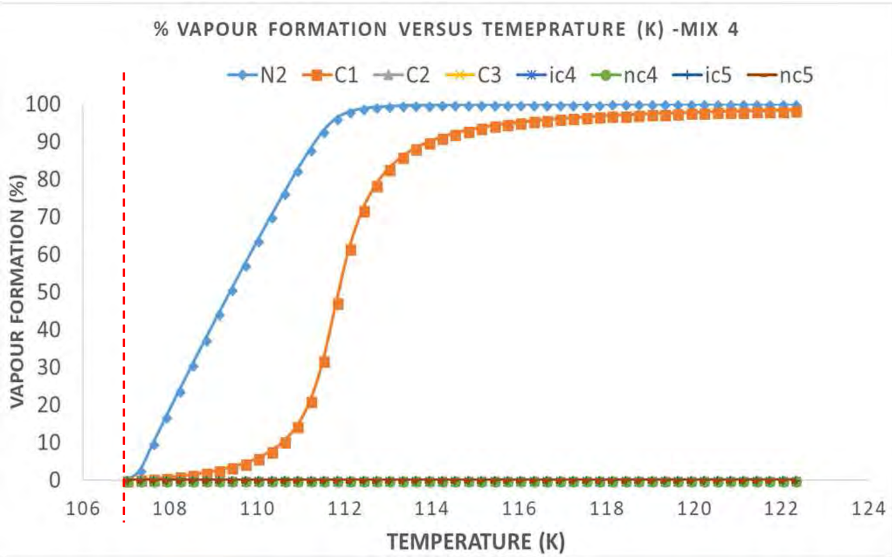
Thermophysical predictions

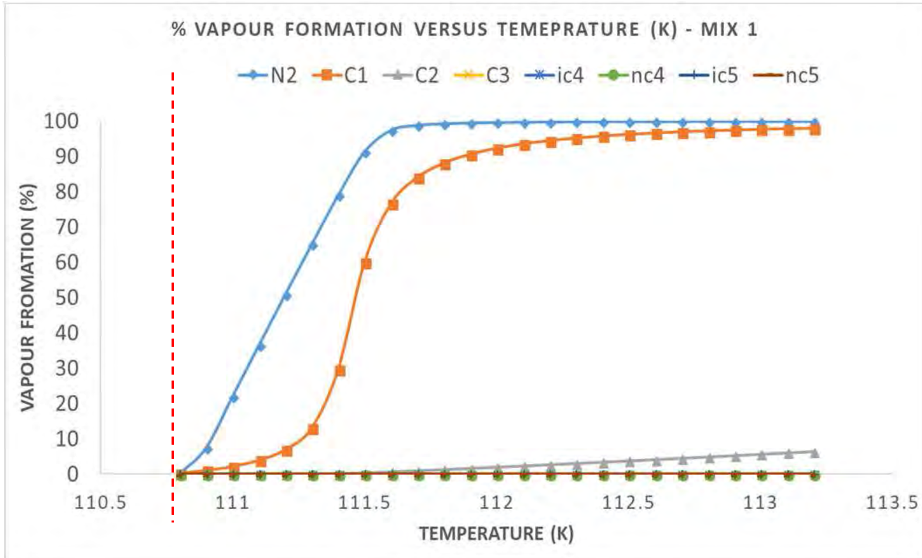
How much gas to add?

	Amount fraction (%mol/mol)			
component	MIX 1	MIX 2	MIX 3	MIX 4
nitrogen	0.60	0.15	1.17	0.04
methane	93.07	98.44	92.63	86.85
ethane	5.48	0.10	2.78	10.65
propane	0.68	0.09	3.03	2.00
iso-butane	0.06	0.63	0.13	0.21
n-butane	0.08	0.43	0.07	0.24
iso-pentane	0.02	0.08	0.10	0.00
n-pentane	0.01	0.08	0.10	0.01
LNG density (g/L)	470.55	459.10	478.48	490.54

Thermophysical predictions

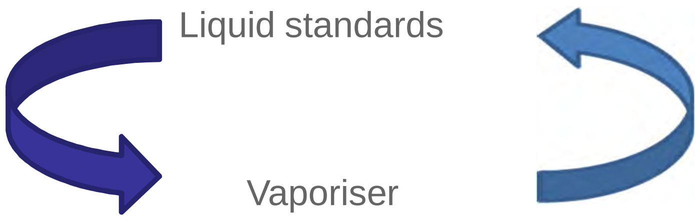
Predicting vapour phase amount of nitrogen and methane





Paradox

- The project was conceived to develop liquid reference standards as there was some concern over vaporiser issues.
- Liquid standards being validated using a GC & vaporiser



Paradox

- The proj … s there
  was son…
- Liquid st…
- Validate
  paradox

BRITISH STANDARD

BS EN 12838:2000

Installations and equipment for liquefied natural gas — Suitability testing of LNG sampling systems

Vaporiser suitability criteria

Values for mass CV, gas density and LNG density taken from Table 1 of EN 12838

			Continuous sampling	
Class	Physical property	Typical value	Maximal random error	Maximal systematic error
A	CV in kJ/kg	53948	9.0	Not significant
	Gas density kg/m^3	.7858	$3.0*10^{-4}$	
	LNG density kg/m^3	494.76	0.15	
B	CV in kJ/kg	53948	18	11
	Gas density kg/m^3	.7858	$6.0*10^{-4}$	$5.0*10^{-4}$
	LNG density kg/m^3	494.76	0.30	0.20

E_n Number

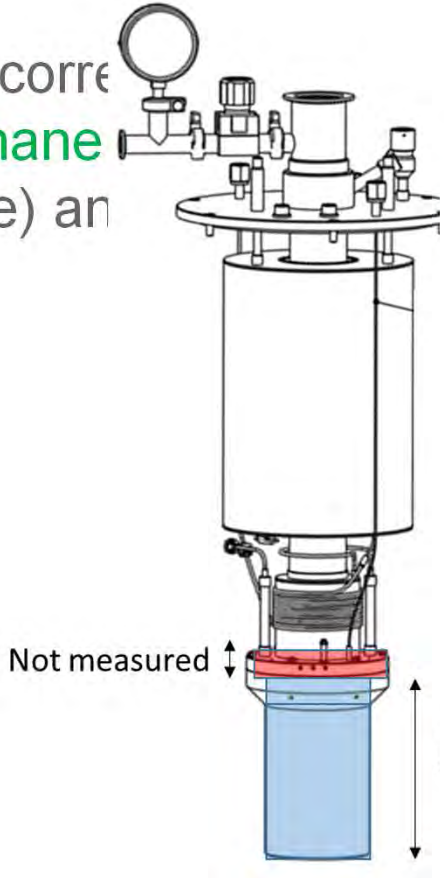
- Agreement between measured and reference values is quantified through the E_n number, which divides the difference in values by the combined uncertainty

$$E_n = \frac{meas - Ref}{\sqrt{U_{meas}^2 + U_{Ref}^2}}$$

- An E_n value of 1 or less shows that the measured and reference values are in statistical agreement

Nitrogen and methane correction

- The corre[...] values use the measured nitrogen and methane [...] as En ratio consistent with PRGM value) an[...] normalised to 100%



Slide 24

JW1 Diagram to illustrate 2 and c1 in headspace above liquid ... more with higher amount fractions of n2

Joey Walker, 06/06/2018

Example results for one reference liquid composition

mix #4R	gravimetric values		measured (GC) values		Modified values	corrected reference values		difference	difference	difference	EN12838
component	xi	U(xi)	yi	U(yi)	yim	xic	U(xic)	(% relative)	KJ/kg	kg/m3	criteria
nitrogen	1.5635	0.0015	1.5638	0.0257	1.5638	1.5638	0.0129	0.0000			
methane	95.2233	0.0095	95.2232	0.1834	95.2232	95.2232	0.0918	0.0000			
ethane	1.1849	0.0011	1.1907	0.0141	1.1849	1.1851	0.0092	0.0049			
propane	0.7660	0.0008	0.7667	0.0081	0.7660	0.7661	0.0041	0.0009			
iso-butane	0.3855	0.0004	0.3838	0.0051	0.3855	0.3856	0.0031	-0.0044			
n-butane	0.5740	0.0006	0.5713	0.0090	0.5740	0.5741	0.0052	-0.0046			
iso-pentane	0.1469	0.0002	0.1459	0.0032	0.1469	0.1469	0.0018	-0.0063			
n-pentane	0.1552	0.0002	0.1545	0.0036	0.1552	0.1552	0.0019	-0.0046			
GCV (15/15)	53699.87		53700.28			53699.51			0.757813		9
Gas Density	0.728388		0.728316			0.728390				-0.0001	3.00E-04
LNG Density 93K	470.3735		470.3477			470.374715				-0.0270	0.15

Corr = Grav value /100-(sum(c2-c5)) X 100-sum(nitrogen+methane)

EffecTech scope of accreditation (UKAS)

LIQUEFIED NATURAL GAS (LNG) ANALYSERS
Calibration of LNG analysers using reference liquid mixtures

LNG ANALYSERS	amount fraction (% mol/mol)	amount fraction (% mol/mol)	In-house method TM024/UT	Uttoxeter
nitrogen	0.1 to 1.8	0.10 % relative + 0.0065	Calibration of analysers used for direct measurement of liquefied natural gas (LNG) using cryogenically prepared reference liquid mixures	
methane	79 to 100	0.035		
ethane	0.1 to 4 4 to 14	0.30 % relative + 0.001 0.05 % relative + 0.01		
propane	0.1 to 4	0.15 % relative + 0.0015		
iso-butane	0.02 to 1.3	0.25 % relative + 0.001		
n-butane	0.02 to 1.3	0.25 % relative + 0.001		
iso-pentane	0.01 to 0.16	0.50 % relative + 0.0002		
n-pentane	0.01 to 0.16	0.50 % relative + 0.0002		

Upcoming research projects:

1. Testing of densitometers using ultrasonic technology
2. Odorising LNG
3. new design to expand application range

Thank you for listening