Results of pycnometer based experiments at INRIM to measure LNG density

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A novel pycnometer and a cryogenics apparatus were designed and manufactured in support of the EMRP – ENG 03 "Metrology for LNG" to provide accurate density measurements of Liquid Natural Gas and synthetic natural gas mixtures in the liquid region.

Densities of two Synthetic Natural Gas Mixtures have been determined in the temperature range 100 K and 111 K with pressures up to 6 bar (0,6 MPa). An unexpected change in composition of the samples affected the liquid density. Such effect could be due to adsorption in the Titanium surface of gas molecules and to evaporation of the mixture light components.

The Pycnometer SLNG2

The pycnometer comprises two cylindrical bodies machined from a Grade 5 Titanium bar alloy (Ti-6Al-4V): the container (the cell) and the expansion vessel, which have a volume ratio of 1/6. The two cylinders are connected together with a threaded bore-tubing, manufactured to fit a commercially available needle high pressure valve in stainless steel for pressure up to 200 MPa. Another similar valve is used to connect the cell with the filling rig through a Vapor Liquid Equilibrium reservoir (VLE)

Apparatus for volume and density determination

With the pycnometer and the VLE reservoir cooled down by means of liquid nitrogen (LN_2) and with helium He_2 (<30 mbar @ 20 °C) around them in the shield housed in the cryostat, the Syntetic Natural Gas at the critical pressure is condensed into the pycnometer until the VLE is filled. In filling, the density of gas, the flow rate, the pressure and the temperature are measured.

Experimental

Materials: Two samples of synthetic natural gas mixture like LNG were the subject of the present density determination. Both samples were provided by Linde (DE), tested and certified by VSL (NL) and measured by INRiM (IT), as regard density at 20°C and several pressure up to 4 MPa

	Cert.VSL 3222202.1		INRiM	Cert.VSL 3222202.4		INRiM
Component	Mix 1		Density 293 K @ 1 MPa	Mix 2		Density 293 K @ 1 MPa
	mol/mol	U mol/mol	kg/m³	mol/mol	U mol/mol	kg/m³
Methane	0,8789	6E-04		0,8127	6E-04	
Ethane	0,0727	1E-04		0,04756	7E-05	
Propane	0,0292	7E-05	7,9086±0,01‰	0,04886	1E-04	9,0846±0,01‰
n-Butane	0,0161	7E-05		0,0242	8E-05	
i-Butane				0,0245	7E-05	
Nitrogen	0,0035	9E-06		0,0431	7E-05	

Operations

Three quantities have to be measured for the density determination by pycnometer method:

- the weight of the empty pycnometer W_0,
- the weight W_{CH4} of the pycnometer filled with high purity methane (99.9995% - SIAD ITALY), and
- the weight W_{Mix} of the pycnometer filled with the mixture to be tested.

$$\rho(T,p) = \frac{W_{Mix} - W_0}{W_{CH_4} - W_0}\rho_{CH_4}(T,p) + \rho_a$$

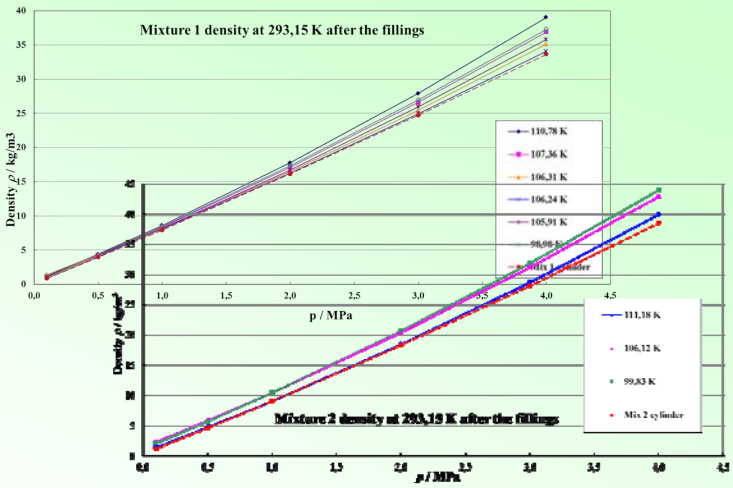
where ρ_a is the density of air during the weighings and ρ_{CH4} (T,p) the density of the reference methane at the filling T and p according to the Refprop values.

Results

When the temperature is about 5 °C below the stated temperature for which the density (volume) has to be measured, the temperature T is stabilized by a PID controller and the pressure p is adjusted on the vapor-liquid equilibrium curve, up to the gas flow rate is about ± 0,05 cm³/min. The observed densities of both mixtures like LNG are highly affected by changes in composition of the samples, in the temperature range between 111,15 K and 99,15K at the pressures between 0,3 MPa and 0,6 MPa. This is shown by the increasing of the gas density at 293 K after the mixtures were liquefied.

Temperature T °C	Temperature T K	Pressure p MPa	Density ρ g/cm³	Uncertainty u_ρ g/cm³	Relative density difference 293 K @ 1 MPa %
-174,166	98,98	0,32	0,514	0,002	6,6
-167,237	105,91	0,49	0,499	0,003	2,6
-165,786	107,36	0,48	0,510	0,001	5,2
-162,374	110,78	0,41	0,506	0,001	8,8

Temperature T °C	Temperature T K	Pressure p MPa	Density ρ g/cm³	Uncertainty u_ρ g/cm³	Relative density difference 293 K @ 1 MPa %
-173,324	99,83	0,59	0,579	0,002	15,6
-167,123	106,03	0,60	0,507	0,003	11,9
-161,972	111,18	0,50	0,488	0,001	0,3



Conclusion

It is observed that different liquid densities can be obtained with different mixture compositions. We suppose that, increasing mixture temperature from melting point and consequently the pressure inside the pycnometer, a flow rate of mixture lighter components is generated along the filling rig, towards outside the pycnometer itself and the VLE reservoir. An additional effect which contributes in composition changing is also the adsorption of heavy molecules by the internal Titanium surface of pycnometer.

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