Laboratory-scale liquefiers for natural gas: A design and assessment study

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Abstract
Exact knowledge of natural gas composition is essential in custody transfer to determine the energy content of the delivery. However, for liquefied natural gas (LNG), a reliable composition determination is difficult. Here, we describe the design of a laboratory-scale reference liquefier that enables the validation and calibration of optical spectroscopy sensors by providing them with a sample of metrologically traceable composition. Hence, it is crucial to avoid fractionation of the sample during liquefaction. This is realized by supercritical liquefaction of a reference gas mixture in conjunction with a special vapor-liquid-equilibrium (VLE) cell. As this is a demanding high-pressure application, low-pressure condensation as liquefaction method was also assessed. Through experimental investigations and VLE calculations, preservation of the composition of the produced liquid sample during condensation was studied. We conclude that under optimized conditions, validation, and calibration measurements of optical sensors can be performed on condensed liquids, which, however, needs further confirmation.

KEYWORDS
composition analysis, liquefaction, liquefied natural gas, optical spectroscopy, vapor-liquid-equilibrium

INTRODUCTION

Challenges due to climate change and the resulting changes in the global energy supply have led to an increased utilization of liquefied natural gas (LNG) in energy transport and storage. Here, reaching higher efficiencies in various fossil fuel processes, including the LNG value chain, can make a significant contribution to continuously reduce the emission of greenhouse gases. In custody transfer, the composition of LNG can vary depending on its origin and even change over time during transport and storage due to gas boil-off. For the determination of the transferred energy, exact knowledge of the composition is essential. It plays a key role in the calculation of calorific value, density, Wobbe Index, and many other properties relevant for trading natural gas. Moreover, the determination of heavy hydrocarbon contents (C6+) in LNG can be important to prevent the formation of solid-liquid equilibria (SLE) and, thus, pipeline blockages. Composition measurements utilizing gas chromatography (GC), however, require sampling and regasification of the LNG, which is known to be prone to errors due to fractionation. Furthermore, a sample withdrawn from pipelines for GC analysis may not represent that of the LNG stream leading to an incorrectly determined amount of transferred energy. Therefore, as an alternative to GC analysis, optical...
spectroscopy probes feature the advantage of online in situ composition analysis by submerging the sensor directly into the LNG transfer line. In this regard, optical measurement principles such as Raman\(^6\) and possibly Fourier-Transform Near-Infrared (FT-NIR) spectroscopy can be used. For validation and calibration measurements, these sensors must be submerged into a liquid LNG-like sample of well-known composition. To obtain such a sample, the cryostat design of the laboratory-scale reference liquefier described within this work is based on a metrologically proven cryogenic single-sinker densimeter,\(^7\)–\(^9\) where reference gas mixtures are liquefied using a supercritical liquefaction technique in conjunction with a special vapor–liquid-equilibrium (VLE) cell. The described design is particularly developed to assess the capabilities of the in situ optical composition measurement systems. (We note that the type of liquefier described here can potentially be used for other types of sensors as well.)

Recently, the development and validation results of a small-scale liquefier were presented.\(^10\) The work demonstrated the performance of the liquefier and metrological traceability of the liquid composition in accordance with the requirements of ISO/IEC 17025.\(^11\) Unlike the design presented in this work, the small-scale liquefier does not utilize supercritical liquefaction but condensation. Since condensation features advantages regarding structural ruggedness and procedural application, it may be conceivable to be adopted for the described liquefier or further measurement facilities. In order to assess the capabilities of condensation as liquefaction technique, comparative density measurements were performed on a laboratory scale using different liquefaction techniques to evaluate the impact on the composition of the liquefied sample.

Further, to understand more comprehensively the current state-of-the-art of predicted properties of LNG in the single phase and in the VLE region, we extend the existing uncertainty analysis of equations of state by a mechanism that propagates the uncertainty of the input parameters, typically temperature, pressure and composition. Currently, the uncertainty of equations of state is typically expressed in terms of the error in the predictions of the relevant properties as compared with experimental data.\(^12\) This contribution aids in more comprehensively characterizing the uncertainty of natural gas properties, which is helpful in the assessment of the performance of liquefaction techniques and applications of (liquefied) natural gas reference data.

2 | GENERAL CONSIDERATIONS AND LIQUEFACTION TECHNIQUES

The conceptual design of the laboratory-scale reference liquefier for natural gases presented in this work is the precursor for the detail engineering of an apparatus, which features preservation and hence metrological traceability in composition; in other words: the composition inside the measuring cell is the same as that of the feed gas. To achieve this preservation, several criteria must be fulfilled, which are determined by thermodynamic and process engineering requirements. Additionally, for suitable validation and calibration measurements, the sensor probes need to be investigated with its field specifications, which implies particular design requirements. Raman and FT-NIR sensor probes are typically mounted to LNG pipelines with flanges that are fitted to a probe shaft of adjustable length for immersion into the homogeneous LNG stream; the characteristic design of such probes is shown in Figure 1. The optical measurement takes place at the tip of the probe shaft. For integration of usual sensor probes, the cryostat of the new reference liquefier has to be adapted to the existing type of mounting. This is important because after the completion of the validation or calibration routines, the sensor has to be installed in the field without further modifications. By this means, the validated/calibrated sensor can either be used for actual composition measurements or as a “gold standard” for comparative calibration measurements of further probes installed in the field.

The validation and calibration measurements have to be performed in the homogenous liquid phase, that is, the probe tip is immersed into a liquid sample of well-known composition. To realize this condition, gravimetrically prepared calibration gas mixtures\(^13\) are liquefied, providing low uncertainties in composition of the reference sample. For the liquefaction of the reference gas, the cryostat of the liquefier must reach the respective temperatures, which are required for the transition from the gaseous into the liquid state. In this regard, equations of state (EOS) such as the GREG-2008 equation of state\(^12,14\) can be used to predict the vapor–liquid phase boundary for specified mixtures and, henceforth, the saturated liquid temperature for a given pressure. Typically, LNG is transported and transferred at temperatures of about 110 K with pressures close to atmospheric pressure. Since very lean natural gases can be present in two phases at these conditions, even lower temperatures might be required depending on the mixture’s composition. To reach these cryogenic conditions, the use of liquid nitrogen (LN\(_2\)) as coolant for the cryostat is required. With a boiling temperature of \(T_{\text{b}}(101.325 \text{ kPa}) = 77.36 \text{ K}\),\(^15\) the components of the cryostat can be efficiently cooled to \(T = 90 \text{ K}\).

Liquefaction on a laboratory scale can be achieved in multiple ways by various filling and cooling procedures of a measurement system. For illustration, Figure 2 shows the vapor–liquid phase boundary of a typical LNG (coming from Norway) in a \(p, T\)-diagram. The homogenous liquid region and the homogenous vapor region are separated by the two-phase region where liquid and vapor coexist. Haynes\(^17\) stated that the composition of the liquid should be slightly different from the prepared mixture, when there is a residual vapor volume

![FIGURE 1 Schematic illustration of optical in situ probes with exemplary probe tips for Raman and FT-NIR spectroscopy sensors](Color figure can be viewed at wileyonlinelibrary.com)
inside a measurement system. Due to the zeotropic behavior of natural gas mixtures, the compositions of liquid and vapor in the VLE are different. Although the overall composition of the fluid will not change in a closed system, any measurements of the liquid sample could provide distorted results, which are not metrologically traceable to the composition of the reference gas mixture. Even if the fluid is completely transferred into the homogenous liquid phase by traversing the two-phase region, a gradient in composition can remain without a homogenization of the mixture (e.g., by mechanical mixing) subsequent to the liquefaction. Accordingly, we recommend that the sample inside the measuring cell is not separating in two phases, neither during the liquefaction nor during the actual measurement. In doing so, maintaining the reference composition for the liquid sample can be ascertained.

Figure 2 indicates two options for the liquefaction. The most straightforward approach is to condense the mixture into the liquid phase by cooling the sample at ambient or slightly elevated pressure (1’ → 2’ in Figure 2). This process can be carried out in two ways regarding the sequence of filling and cooling. Either, the cryostat is filled with the sample at ambient temperature and subsequently cooled down at constant filling pressure, or the evacuated apparatus is being cooled down and then filled with the mixture as soon as the target temperature is reached. Both methods tolerate the formation of a VLE, which can lead to a residual change in composition of the liquefied sample.\(^7\)\(^9\)

The two-phase region can be effectively bypassed when applying a supercritical liquefaction procedure.\(^7\)\(^9\) Here, the cryostat is filled beyond the cricondenbar at ambient temperature (point 1 in Figure 2), which is followed by cooling the cryostat to the target temperature at a supercritical pressure (1 → 2). The pressure can then be reduced by venting substance from the system or by using a pressure adjustment cell.\(^18\) When the pressure falls below the pressure of the cricondenbar, an inevitable phase transition from liquid to vapor will form, when fluid filled components exhibit temperatures above the saturated liquid temperature. This, for example, can be the pressure measurement or the filling line located outside of the cryostat or even tubing at elevated temperatures within the cryostat. To prevent an impact on the liquid sample under investigation, this phase transition and its related component fractionation must be considered accordingly.\(^7\)\(^9\) Hence, by appropriately utilizing this supercritical liquefaction procedure, the composition of the feed gas can be maintained in the homogeneous liquid phase, which is exactly the primary task of a reference liquefier. But even when the reference mixture is liquefied without a change in composition, it must be ensured that sorption phenomena, stratification of the liquid sample and diffusion effects that also can lead to changes in the composition are mitigated accordingly. Regarding the requirements of the liquefier, however, the supercritical technique involves the system to withstand high pressures to be able to exceed the pressure of the cricondenbar which, for natural gas mixtures, typically is between 5.0 and 9.0 MPa. Hence, to facilitate the supercritical liquefaction for most common LNG mixtures, a pressure rating of the liquefier of at least 10 MPa is recommended. In contrast, just a slight overpressure is required when condensing the sample. This implies that building a liquefier employing condensation as liquefaction technique can be less expensive.

3 | Conceptual Design of the Reference Liquefier

3.1 | Basic design

The design of the core-apparatus as shown in Figure 3 is based on the cryogenic single-sinker densimeter developed and improved by Richter and colleagues,\(^7\)\(^9\) that is, adopting the application of supercritical sample liquefaction in conjunction with a VLE-cell.\(^7\)\(^9\) The apparatus involves a multi-layer vacuum insulation to reduce the heat flow from the environment into the cryogenic sections. The tip of the sensor probe is submerged into the measuring cell, which is suspended from an intermediate plate. This plate is attached to the base plate of the cryostat. A copper shield is installed at the intermediate plate to enclose the measuring cell and shield it from thermal radiation.

A so-called VLE-cell is connected to the measuring cell to realize the functional principle that was developed for the cryogenic single-sinker densimeter.\(^7\) The VLE-cell is located at the same height as the intermediate plate. By forcing the phase boundary of the VLE to occur inside this cell, the phase transition, and the distorting impact on the composition of the liquid is removed from the measuring cell. In addition, the VLE-cell can be used to adjust the pressure of the entire system subsequent to filling the apparatus. For a detailed description of the application and functional principle, please see references.\(^7\)\(^9\)

As can be seen in Figure 3, the mounting flange of the pilot probe under study is attached to the base plate of the cryostat. The probe shaft is connected to the measuring cell using a special hollow screw, which is used to compress a set of gaskets into the measuring cell and around the probe shaft. This design enables a relatively easy assembly and disassembly of the sensor. Once the vacuum cylinder and the insulation shield are removed and the hollow screw is loosened, the probe can be simply pulled out of the cryostat.
3.2 Temperature control

The cryogenic conditions with temperatures as low as 90 K require an adequate cooling solution, which is capable of providing a constant sample temperature within few millikelvins. As mentioned above, liquid nitrogen is used as coolant. For the concept presented here, three individually controllable ring-thermostats are fitted to the measuring cell, the VLE-cell, and the intermediate plate, respectively. The main parts of these modular ring-thermostats are a liquid nitrogen fed copper coil for cooling and a controlled electric resistance heater for fine temperature adjustments. As an example, Figure 4 shows a schematic cross section of the ring-thermostat installed at the intermediate plate. The mounts for the copper coil and the heater element are attached to the thermostat base ring either by soft-soldering or by screwing together with (vacuum resistant) low-temperature thermal grease; all components are made of copper to optimize the conduction of heat. The contact area of base ring (thermostat bracket) and intermediate plate should also be treated with thermal grease. To ensure sufficient heat dissipation, the heat-conducting cross-sectional areas as well as the contact surface to the LN₂ within the coils have to be dimensioned accordingly.

The setup of three independent ring-thermostats allows to set different target temperatures for the measuring cell, the VLE-cell, and the intermediate shield, which is an essential precondition to utilize the supercritical liquefaction procedure. The measuring cell is set to a temperature in the homogenous liquid region, while the VLE-cell is generally held at higher temperatures making sure that the liquid to vapor phase transition occurs inside this auxiliary cell. In contrast, the
intermediate plate temperature is set \( \sim 9 \) K below the temperature of the measuring cell. This temperature difference provides the measuring cell with passive cooling during steady-state operation. Therefore, no liquid nitrogen is required, and the temperature is solely controlled by the resistance heater, which results in only small temperature oscillations as small as a few millikelvins. Furthermore, unwanted heat flows into the measuring cell can be trapped by targeted thermal bridging (e.g., by contacting the probe shaft with the intermediate plate, see Figure 3). Thereby, potential partial evaporation can be prevented when the state of the liquid sample is close to the saturated liquid line. Realization of only small temperature oscillations is also important to maintain constant pressure. The reason is as follows: when the filling of the measuring system is completed during the overall liquefaction procedure (Point 2 in Figure 2), the sample inlet is closed with the apparatus becoming an isochoric system. Consequently, due to the low compressibility of the liquid phase, small fluctuations in temperature can give rise to substantial variations in pressure. If it is required to provide very stable pressures during validation or calibration measurements, it is also recommended to thermostatically control the piping outside the cryostat or to reduce the impact of variations in ambient temperature via thermal insulation. Moreover, well-controlled temperature and pressure conditions can prevent a potential distortion of the measured spectra of the optical sensors, which can show a relevant dependency on temperature and pressure.\(^1\)\(^9\) Given this interrelationship, we recommend to perform calibration-validation measurements at field conditions. However, this requires the cryostat to cover a certain range in pressure and temperature including different modes of temperature control (e.g., rough to fine).

### 3.3 Thermal design calculations

The dimensioning of the described reference liquefier is based on a thermal analysis. Using a parametric and simplified model for the core apparatus, all decisive heat flows between internal components and the environment were calculated depending on the set-point temperatures of the three ring-thermostats.\(^2\)\(^0\) These calculations include not only the occurring heat flows but also the resulting temperature gradients along the intermediate shield and the measuring cell using an iterative method. Evaluating the temperature gradient along the intermediate shield is crucial to assess the passive cooling of the measuring cell as described further above. The temperature gradient along the measuring cell should be kept to a reasonable degree to avoid vortices inside the cell and to obtain a representative temperature measurement. This is especially relevant when measurements are carried out close to the saturated liquid line as vaporization of the sample has to be definitely avoided.

To assess the temperature range required for validation and calibration measurements, a parametric study has been performed with measuring cell temperatures ranging from 100 to 160 K. Accordingly, the temperature of the intermediate plate was set to temperatures of 91 to 151 K, while the temperature of the VLE-cell was varied within (20 to 110) K above the measuring cell temperature to account for different heat flow scenarios. The study showed that the temperature gradient along the intermediate shield is in the range of 5.5 to 7.5 K due to the heat input from the outer insulation cylinder, which was assumed to be at ambient temperature. The gradient along the measuring cell turned out to be within 10 to 20 mK, where the variation is caused by the constant 9 K subcooling of the intermediate plate. By adjusting the subcooling of the intermediate plate to the prevalent temperature gradient along the intermediate shield, the gradient along the measuring cell could be kept almost the same for all temperatures of the measuring cell.

Regarding the overall cooling demand, less than 50 W are required for the cryostat with the dimensions determined from the different scenarios. This relates to an approximate liquid nitrogen consumption of less than 30 dm\(^3\) per day for steady-state operation. For the initial cooling of the cryostat from ambient temperature to the target temperatures, that is, the liquefaction of a gaseous sample, less than 25 dm\(^3\) are required for all scenarios. These values refer to the dimensions we selected for the present cryostat concept; they will of course change with a variation of the design.

Depending on the sensor requirements regarding stability in temperature during calibration, it might be feasible to utilize a simplified insulation layout. Hence, in addition to the cryostat described above, two alternative designs were investigated within the scope of the thermal design calculations. First, active cooling of the intermediate shield could be dropped so that it solely serves as radiation shield. As a result, the measuring cell has to be actively cooled with liquid nitrogen, and the temperature gradient caused by larger heat flows increases significantly to 550 to 820 mK. Second, the cryostat can be further simplified leaving out the intermediate shield. For this setup, the calculated temperature gradient along the measuring cell exceeds 1,400 mK. Consequently, both designs should only be considered, if the corresponding gradients can be tolerated. When measurements are carried out in sufficiently subcooled liquid states, greater temperature gradients along the measuring cell might not be an issue. Nevertheless, we note that that the thermodynamic models used for calculation of the phase boundary is also subject to uncertainty, that is, this circumstance has to be taken into account within the design process of a liquefier.

## 4 ASSESSMENT OF CONDENSATION FOR LIQUEFACTION

### 4.1 Experimental investigations

To realize the recommended supercritical liquefaction technique, which was developed to maintain the feed composition,\(^7\)\(^-\)\(^9\) a quite elaborate apparatus has to be set up that can be expensive depending on the ultimate design and the selection of periphery. As discussed before and shown in Figure 2, another way of liquefaction is possible, namely via condensation. The development and first results of a facility for producing LNG samples based on this technique were recently reported by Walker et al.\(^1\)\(^0\) Even though the optical pilot probes are
typically able to withstand high pressures, using condensation implies the advantage that no high-pressure technology is required. For this procedure, however, at least a temporary fractionation of the mixture during the transition from gas to liquid (i.e., when crossing the two-phase region) will occur. Hence, for metrological purposes, the impact of the temporal fractionation on the composition of the liquid sample inside the measuring cell needs to be clarified. Predicting a change in composition based on this liquefaction technique for such a dynamic system with numerous input factors is not possible with the accuracy required for a reference liquefier. Hence, to assess the extent to which the feed gas composition is preserved for the liquefied sample, it is partially reevaporated and analyzed using gas chromatography. A point of attention when scrutinizing the data from such a validation concerns the sampling and regasification itself, which is an extra variable, and as already mentioned, fractionation is also a potential issue here.

The experimental investigations in our work allow a direct estimation of a shift in the composition of the liquid without the need of regasification. This is done utilizing the cryogenic single-sinker densimeter with an operational temperature range of 90–300 K at pressures of up to 10 MPa, facilitating supercritical liquefaction as well as condensation of reference gas mixtures. Conducting accurate density measurements at the same \((T, p)\) state points for both liquefaction techniques enables the observation of a possible change in density caused by condensation. By using a binary mixture for these investigations, a change in density can be directly traced back to a change in composition. The magnitude of this change can then be estimated employing an accurate equation of state. Here, we used a binary reference gas mixture composed of \((0.98017 \pm 0.00150)\) mol/mol methane and \((0.01983 \pm 0.00016)\) mol/mol iso-pentane (for details regarding the uncertainty in composition, please see the supplementary material). Hence, the EOS-LNG equation of state as an enhancement of the GERG-2008 equation of state with improvements regarding butanes and pentanes is used for the determination of the change in composition. The required reference densities were determined using the supercritical liquefaction technique. In order to gain a more comprehensive understanding of the impact of condensation on the liquid composition, different approaches of condensation were studied.

Concerning the filling and cooling sequence, two scenarios were experimentally assessed. Firstly, the apparatus was evacuated and cooled to the target temperature prior to the actual filling that was conducted at a constant pressure. However, with a precooled system, the rapid liquefaction of the introduced sample impedes to fill at a constant pressure. In practice, the measured pressure fluctuated within \(\pm 0.05\) MPa during the filling of the apparatus. Secondly, the system was pressurized at room temperature and then isobarically cooled to condense the sample during the temperature reduction. Both approaches were tested at filling pressures of \(\sim 0.3\) and \(1.0\) MPa to consider a potential influence of the pressure during condensation. This strategy is based on the circumstance that component fractionation in VLE amplifies at higher pressures due to the higher vapor density, even for systems of same volumetric vapor fraction.

The different condensation procedures, four in total, were each carried out at a measuring cell temperature of 110 K. The temperature of the densimeter’s VLE-cell was at 250 K and, thus, well above the saturated vapor temperature so that the phase transition from vapor to liquid is located in the connection line between the measuring cell and the VLE-cell. At a temperature of 110 K, no direct reference densities are available; therefore, the data measured by Eckmann et al at 100 and 120 K were fitted to a quadratic polynomial and then interpolated to obtain the densities at \(T = 110\) K. To consider the nonlinear relationship between density and temperature, the interpolation was not carried out using absolute density values but relative deviations of the reference densities from the EOS-LNG equation of state, which is capable of representing the temperature dependency of density with reasonable accuracy. For each of the four fillings carried out in this work, density measurements at different pressures were performed. The pressure after each measurement was reduced by venting substance from the system since the functionality of the VLE-cell for pressure control is not available when only filled with gaseous sample.

As can be seen in Figure 5, the relative deviations of the experimental densities \(\rho_{\text{exp}}\) from the interpolated reference densities \(\rho_{\text{ref}}\) reveal that the condensation of sample into the precooled and evacuated measuring cell resulted in a slight decrease in density, which implies an enrichment of methane in the liquid phase. Nevertheless, the shift in experimental density is within the relative expanded uncertainty \((k = 2)\) of the experimental reference densities of less than \(0.015\%\). We note that the uncertainty in composition of the reference gas mixture is excluded in this combined uncertainty because exactly the same mixture sample was used for the

![Figure 5](wileyonlinelibrary.com)

**FIGURE 5** Relative deviations of experimental densities \(\rho_{\text{exp}}\) at \(T = 110\) K measured after condensation of the sample from reference densities \(\rho_{\text{ref}}\) interpolated using experimental densities at \(T = 100\) and \(120\) K measured after supercritical liquefaction of a binary \((0.98017\) methane +0.01983 iso-pentane) mixture. \(\triangle\) filling to \(p = 1.0\) MPa prior to cooling; \(\bigcirc\) filling to \(p = 0.3\) MPa prior to cooling; \(\times\) condensation at \(p_{\text{ref}} = 1.0\) MPa into the precooled, evacuated measuring cell; \(\bigtriangleup\) condensation at \(p_{\text{ref}} = 0.3\) MPa into the precooled, evacuated measuring cell; grey area, expanded uncertainty of the experimental reference densities \(U(\rho_{\text{ref}}) = 0.015\% (k = 2)\) without the contribution of the uncertainty in composition of the reference gas mixture. Details on the composition of the mixture are given in the supplementary material [Color figure can be viewed at wileyonlinelibrary.com]
condensation experiments within the present work as for the reference measurements by Eckmann et al. Nevertheless, due to the consistency of the data, neither a change in composition caused by the condensation procedure nor a dependency on the filling pressure can be observed, which supports the findings of Walker et al.

The condensation procedure where the system was pressurized at ambient temperature, however, resulted in a stronger decrease in density clearly exceeding the uncertainty of the reference densities. The change in composition can be estimated by iteratively changing the composition for the densities calculated with the EOS-LNG equation of state to gain relative deviations of the experimental densities in the same order as for the reference densities. Here, a change in methane amount fraction of ~0.0003 and 0.0004 could cause the observed decrease in density of the liquid phase for the filling pressures of (1.0 and 0.3) MPa, respectively. We explain this decrease in density as a result of the rather slow condensation during the cooling of the system, which presumably forms a liquid phase highly enriched with iso-pentane at the bottom of the densimeter’s measuring cell during the presence of a VLE. Accordingly, when the condensation is completed, the liquid phase at the height of the densimeter’s sinker exhibits a reduced fraction of iso-pentane when the fluid is not being homogenized. Even though the sinker of the densimeter is repeatedly moved throughout the entire investigation, for this specific fluid, the remixing of the liquid is a protracted process. As shown in Figure 5, the density slowly increases over time, when the system is kept at the same conditions, presumably caused by iso-pentane gradually being mixed into the fluid that is surrounding the sinker. A reference liquefier does not involve a vertically moving sinker inside the measuring cell, thus, utilizing a mixing system such as a magnetically-coupled stirrer at the bottom of the measuring cell would be possible to compensate for a local composition gradient of the liquefied sample.

We hypothesize that stratification of the reference fluid was not observed for the condensation approach with a precooled measuring cell because the actual liquefaction only takes few minutes until the measuring cell is completely filled with liquid instead of up to 4 hr as for the other approach. Hence, the high flow rate of the introduced sample most likely causes a sufficient circulation within the measuring cell, preventing the accumulation of a liquid phase rich in iso-pentane at the bottom of the measuring cell. Theoretically, the observed change in density over time can be caused by the liquid to vapor transition located in the connection line to the VLE-cell as well. However, this behavior cannot be observed for the condensation procedure with precooled measuring cell and, therefore, can be assumed to be negligible at least for measurement periods of less than 1 day per filling.

In addition to the above described experimental investigations, further examinations were carried out to evaluate the magnitude of sample liquefaction taking place outside of the measuring cell. In this regard, the condensation with precooled measuring cell was once again performed with the VLE-cell temperature now set to the homogeneous liquid region, this time with a measuring cell temperature of 140 K. This condition causes condensing within measuring cell and VLE-cell simultaneously, which consequently results in liquid formed in the VLE-cell being flushed into the measuring cell, accumulating the heavier components. Upon completion of the condensation, the VLE-cell was completely filled with liquid. The density measurements subsequent to this liquefaction procedure using the same (0.98017 methane +0.01983 iso-pentane) mixture resulted in a significant increase in density in the range of 0.125% (see Figure 6) compared with the reference densities. Again, using the EOS-LNG equation of state for estimation, now an enrichment in iso-pentane amount fraction of 0.00047 would cause this observed increase in density. This magnitude is within the typical standard uncertainty of the optical spectroscopy measurements of at least 0.0010 amount fraction, but would certainly become a relevant contribution to the combined uncertainty of the calibration measurement. In order to verify these findings for an actual use case, the same procedure was applied to a multicomponent mixture representing a typical LNG coming from Norway (see Table 1 for composition) at a measuring cell temperature of 135 K. Here, an increase in density of ~0.127% compared with reference densities was observed. Due to the number of degrees of freedom in composition, however, this change in density cannot be uniquely traced back to a change in composition. An analytical determination of the liquid composition via GC is not feasible as the combined uncertainty of sampling, sample vaporization and GC analysis would exceed the uncertainty of the feed gas composition. Hence, VLE flash calculations with the EOS-LNG equation of state were used for an approximate ratio of the change in liquid composition for each component. For example, when applying these ratios, the observed increase in density could be the result of a change in composition according to Table 1. Here, the change in amount fraction represents the ratios estimated with the flash calculations. With absolute changes in composition of up to 0.00139 amount fraction, the uncertainty in composition measurement is somewhat exceeded.

### 4.2 Uncertainty analysis using fluid phase equilibrium calculations

The current state-of-the-art in evaluating the performance of equations of state does not go beyond describing their ability to represent experimental data. The metric often used is the relative error (deviation) between prediction and experimental value. Such a characterization of the equation's uncertainty is incomplete and for many applications of calculated values unsatisfactory. Sometimes, there is a valid motivation of excluding a particular source of uncertainty as in the comparison of the densities measured when comparing various liquefaction methods, where the liquid was in all cases obtained from the same reference gas mixture (see previous section).

For most real-world applications, a comprehensive uncertainty evaluation is needed, which includes the uncertainty of all input quantities concerned. Considering complicated models like equations of state, it is not straightforward to use the law of propagation of uncertainty from the Guide to the expression of Uncertainty in Measurement (GUM) for this purpose. Furthermore, this mechanism only provides reliable results when the model is (approximately) linear.
and the uncertainties of the input quantities are small. A more versatile mechanism propagates the probability density functions assigned to the input quantities using the model to obtain the probability density function of the output quantities. This mechanism often involves the use of a Monte Carlo method to sample from the input distributions for creating a sample of the output distribution. From this output distribution, the value, standard uncertainty (standard deviation) and coverage interval, among other, can be obtained.

In previous work, an uncertainty evaluation was described for a flash calculation. The models used to describe the liquid and vapor phase properties were kept very simple. In this work, the GERG-2008 equation of state was used for the flash calculations. This calculation was implemented in the TREND 4.0 software. The calculation is treated as a black box in this uncertainty evaluation. For the modeling of the liquefier, it is relevant to know the uncertainty of the difference \( x - z \) where \( z \) denotes the feed composition and \( x \) the liquid composition. The feed composition is taken as the composition of the reference gas mixture being liquefied. From this composition, the uncertainty is available.

The measurement model in this instance is primarily the GERG-2008 equation of state in combination with the algorithm used. A convenient way to perform an uncertainty evaluation using a measurement model that is in the form of an algorithm is the use of the Monte Carlo method from GUM Supplement 1 (GUM-S1) or GUM Supplement 2 (GUM-S2). The principal difference between the two methods is that the method of GUM-S1 is suited for a univariate measurement model, whereas that of GUM-S2 is suited for a multivariate measurement model. The difference \( x - z \) is an example of a multivariate measurement model, hence the Monte Carlo method of GUM-S2 should be used. In previous work, a simple example of using the Monte Carlo method in the combination with an iterative calculation has been given to calculate the VLE properties of a pure fluid using a simple cubic equation-of-state.

The Monte Carlo method can be implemented as follows:

1. Choose the number of Monte Carlo trials \( M \)
2. Assign a (multivariate) probability density function to the input quantity \( z \)
3. Repeat \( M \) times the following steps
4. Generate a composition \( z^k \)
5. Perform the flash calculation to obtain the corresponding \( x^k \)
6. Calculate the difference \( x^k - z^k \)
7. Calculate the mean of the differences \( x^k - z^k \) as estimate of the difference between the liquid and feed composition
8. Calculate the covariance matrix of the differences \( x^k - z^k \) to obtain the standard uncertainties of the differences in the amount fractions of the components

Whereas the implementation of the Monte Carlo method by itself is quite straightforward, there is one complicating factor, namely the

**FIGURE 6** Relative deviations of experimental densities \( \rho_{\text{exp}} \) from densities \( \rho_{\text{calc}} \) calculated with the EOS-LNG equation of state, experimental reference densities based on a supercritical liquefaction for the (0.98017 methane +0.01983 iso-pentane) mixture at \( T = 140 \text{ K} \) (left) and LNG Norway at \( T = 135 \text{ K} \) (right); \( \rho_{\text{exp}} \) experimental densities of a condensed liquid mixture with the VLE-cell filled with liquid; the filling pressure of both condensation series was 2.0 MPa [Color figure can be viewed at wileyonlinelibrary.com]

**TABLE 1** Compositional change of the liquid phase after condensation of LNG Norway derived by flash calculations using the EOS-LNG based on the change in experimental density

| Component   | Calibrated reference amount fraction | Modified amount fraction | Change in amount fraction |
|-------------|-------------------------------------|--------------------------|--------------------------|
| Methane     | 91.798 \( \times 10^{-2} \)          | 91.666 \( \times 10^{-2} \) | \(-0.132 \times 10^{-2} \) |
| Ethane      | 5.698 \( \times 10^{-2} \)           | 5.837 \( \times 10^{-2} \) | 0.139 \( \times 10^{-2} \) |
| Propane     | 1.303 \( \times 10^{-2} \)           | 1.337 \( \times 10^{-2} \) | 0.034 \( \times 10^{-2} \) |
| Butane      | 0.396 \( \times 10^{-2} \)           | 0.406 \( \times 10^{-2} \) | 0.010 \( \times 10^{-2} \) |
| Nitrogen    | 0.805 \( \times 10^{-2} \)           | 0.754 \( \times 10^{-2} \) | \(-0.051 \times 10^{-2} \) |
feed composition. Whereas it is relatively uncomplicated to assign a (multivariate) probability density function to a composition, it is not straightforward to sample from it. A composition can be best described as a vector (array) of fractions, which add to a constant.\textsuperscript{28} Hence, the covariance matrix associated with this vector is singular, which causes difficulties in many algorithms for the generation of pseudo-random numbers. This problem has been known for a long time\textsuperscript{29} and has been investigated by several authors.\textsuperscript{30,31}

The problem of the singular covariance matrix can be “solved” in several ways. Firstly, a composition can be generated from a submatrix of the covariance matrix, for example by leaving the amount fraction methane out, and calculating the amount fraction methane by difference. This is a rather naive solution to the problem but might work if the uncertainty associated with the amount fractions is small. A second solution would be to use the pseudo-inverse of the covariance matrix rather than the inverse of the covariance matrix in, say, a multivariate normal distribution. A third solution, based on the results of compositional data analysis,\textsuperscript{31,32} would be to use a log-ratio transformation. With the isometric log-ratio transformation, the Euclidian distances between compositions are retained, and this is the only transformation that produces a nonsingular covariance matrix. On the transformed composition, the multivariate normal distribution can be used. After drawing a sample from this distribution, the sample can be converted into a composition by the inverse of the isometric log-ratio transformation.

When using compositions with small (relative) standard uncertainties, it is expected that when using these to generate compositions, the generated compositions will have small deviations from the mean composition fed into the random number generator. In the naive case, the generated compositions will not satisfy the constraint that all amount fraction should add to a constant. The latter can be achieved by normalizing the compositions thus generated, for example, the procedure from ISO 6974-1.\textsuperscript{28} The corrections made to the amount fractions will then be generally small. The standard uncertainties that are achieved by national metrology institutes (NMIs) in comparisons of national measurement standards (“key comparisons”\textsuperscript{33-35}) are a suitable basis for this uncertainty evaluation, as they are the best uncertainties achievable. They range from below 0.0010 for the amount fraction methane to 0.0050 for the amount fraction hexane.

We have used the described mechanism to explore how the uncertainty of the feed composition propagates in a flash calculation. We did so for a number of different LNG-compositions. Temperature and pressure were kept constant but could have been included in the uncertainty evaluation as well. The results for one of the compositions (0.008 nitrogen, 0.918 methane, 0.057 ethane, 0.013 propane, 0.0017 iso-butane, 0.0015 n-butane, 0.0004 iso-pentane, and 0.0004 n-pentane) is shown in Table 2. The results are based on a rather small sample of the output distribution ($M = 1,000$), but this sample size is sufficient to reproduce the first two digits of the stated SD.

Most of the relative standard uncertainties of the amount fractions in both phases are approximately equal to the relative standard uncertainties assigned to the corresponding amount fractions in the feed composition. Only for methane, an effect is seen due to the application of the normalization constraint (all amount fractions sum up to unity). This effect becomes more prominent with higher amount fraction methane.

This mechanism for propagating measurement uncertainty can also be applied on other quantities calculated from the equation of state such as density, internal energy, enthalpy, and free energy. For a comprehensive propagation of uncertainty, also the parameters of the equation of state should be included in the evaluation process. If there are no meaningful systematic effects of the model to be accounted for, then this mechanism provides a comprehensive evaluation of the measurement uncertainty.

### 4.3 Evaluation of results

Our experimental investigations revealed that, under optimized conditions, condensation can be used to prepare a liquid of known composition and, hence, can potentially be used for validation and calibration measurements of optical sensor probes. The comparative density measurements showed no significant change in composition, when condensing the reference gas mixture into a precooled and evacuated measuring cell as long as no liquid is formed elsewhere in the system but the measuring cell. However, it was also shown that this capability can quickly cease if the overall system or procedure do not consider the outlined pitfalls. The finding that this way of condensing a sample mixture did not cause a demonstrable distortion of the liquid composition is only valid for the utilized single-sinker densimeter, and it cannot be assumed that it is directly applicable to other systems. The single-sinker densimeter allows for high-precision

| Component | $z$ | $u(z)/z$ | $x$ | $u(x)/x$ | $y$ | $u(y)/y$ |
|-----------|-----|-----------|-----|-----------|-----|---------|
| Nitrogen  | 0.79999 | 0.07% | 0.00258 | 0.07% | 0.82708 | 0.07% |
| Methane   | 91.79998 | 0.006% | 6.77321 | 0.002% | 94.68872 | 0.003% |
| Ethane    | 5.70001 | 0.08% | 44.77681 | 0.06% | 4.372391 | 0.07% |
| Propane   | 1.30002 | 0.09% | 36.32528 | 0.07% | 0.110054 | 0.07% |
| Iso-butane| 0.17000 | 0.11% | 5.13676 | 0.12% | 1.2612 $10^{-3}$ | 0.13% |
| Butane    | 0.15000 | 0.11% | 4.55167 | 0.12% | 4.6010 $10^{-4}$ | 0.12% |
| Iso-pentane | 0.04000 | 0.24% | 1.21722 | 0.26% | 6.6498 $10^{-6}$ | 0.26% |
| Pentane   | 0.04000 | 0.26% | 1.21722 | 0.26% | 6.6498 $10^{-6}$ | 0.26% |

**TABLE 2** Compositional uncertainty of a flash calculation of an LNG mixture at $T = 150$ K and $p = 0.1$ MPa; feed composition ($z$), liquid composition ($x$), and gas composition ($y$) are expressed in amount fractions (%)
control of the fluid's thermodynamic conditions. Consequently, by means of appropriate process conditions, it can be ensured that no condensation occurs outside the measuring cell which, moreover, can be monitored via the multiple temperature measurement sites of the densimeter. In addition, the continuous movement of the sinker did not allow for prompt remixing of a distorted liquid composition, but ensures that no stratification is formed when a homogenous sample is present after liquefaction. Whether a substitute for the vertically moving sinker inside the measuring cell, for example, a magnetically-coupled mixing system, is required depends on the residence time of the liquefied sample in the measuring cell during the calibration and validation measurements of optical sensors. Our experience from density measurements of cryogenic liquid mixtures shows that a liquefied sample does not change composition to such extent that density would shift noticeably, even after several hours without moving the densimeter's sinker. Hence, a stirrer is not necessarily required for a reference liquefier in case (a) the liquefaction technique maintains the composition of the reference gas mixture, (b) liquefaction involves some turbulence, and (c) the liquefied sample has only relatively short residence times in the measuring cell, for example, few hours.

The investigations within this work showed that the phase transition within the connection line between measuring cell and VLE-cell did not seem to exert any influence on the investigations in this work. Here, we note that the inner diameter of the tubing with 1.8 mm creates an extremely small volume in which condensation actually takes place outside the measuring cell. Due to the large temperature gradient between measuring cell and VLE-cell, the phase transition from liquid to vapor was located only few centimeters above the top of the measuring cell. Additionally, the small diameter of the tube also inhibits diffusion, which would change the composition over time, an effect that was extremely minimized by appropriate modifications of the single-sinker densimeter.

Considering that one should be very mindful with transferring the presented results to other experimental setups and different mixtures, the uncertainty analysis of LNG flash calculations came to the result that most of the relative standard uncertainties of the amount fractions in both phases are approximately equal to the relative standard uncertainties assigned to the corresponding amount fractions in the feed composition, except for methane. As a consequence, when experimental temperature, pressure and the reference sample composition as input variables for a thermodynamic equation as well as the vapor space in the respective liquefier are accurately known, we suppose that a state-of-the-art fundamental equation of state can be used to reliably estimate the composition of the liquid phase. This is particularly helpful when condensation is used for liquefaction but also here, the experimental setup impacts this consideration as the vapor fraction of the VLE across the liquefier has to be precisely known.

5 | CONCLUSIONS

In this paper, the conceptional development of a small-scale reference liquefier for cryogenic liquid mixtures such as LNG is described. The resulting design may serve as the precursor for the detail engineering of an apparatus that features traceability in composition, which is an essential prerequisite, for example, for the validation and calibration of optical composition measurement systems. To assess the capabilities of the in situ optical composition measurement systems often used in industrial oil and gas applications, the apparatus was specifically designed to adopt the field mounting solution of the sensor probes. The sophisticated design of the cryostat allows operation over wide temperature and pressure ranges in the liquid region enabling calibration/validation measurements close to field conditions.

Thermal calculations for a large combination of temperature set points of the measuring cell, the VLE-cell and the intermediate plate, were the major input to dimensioning the apparatus. As a result, a temperature gradient along the measuring cell of less than 20 mK can be achieved, which is certainly a good basis for calibration/validation measurements. If allowed by the technical specifications of the sensor regarding stability in temperature during calibration, we showed that the thermal design can be specifically simplified.

To confirm if condensation as liquefaction technique might be a reasonable alternative to supercritical liquefaction of a reference mixtures, density measurements of condensed liquids were carried out. The experimental densities were compared with reference densities of the same mixtures that were measured using a reference densimeter. It was found that the change in composition of the liquid phase was only small when the sample was filled into the precooled and evacuated system. Here, the deviations from the reference data were within the experimental uncertainty of the reference densimeter. Thus, as for the studied circumstances it can be stated that the given condensation procedure is capable of liquefying gas mixtures without a relevant change in composition. Nevertheless, we note that this result is not universally valid but needs to be proven with different experiments and especially further LNG-like mixtures containing nitrogen and heavy hydrocarbons.

Finally, an elaborate uncertainty analysis of LNG flash calculations using state-of-the-art fundamental equations of state for mixtures based on a Monte Carlo method revealed that the uncertainty of the predicted composition of the coexisting phases is on the same order as for the feed mixture. This observation might be a useful input for the uncertainty analysis of liquefiers that are based on condensing a gas mixture of well-known composition.

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AUTHOR CONTRIBUTIONS

Nils von Preetzmann: Conceptualization; data curation; formal analysis; investigation; methodology; project administration; validation; visualization; writing—original draft; writing—review and editing. Philipp Eckmann: Conceptualization; investigation; methodology; project administration; supervision; writing—original draft; writing—review and editing. Adrian van der Veen: Conceptualization; data curation; formal analysis; investigation; resources; software; supervision; writing—original draft; writing—review and editing. Jianrong Li: Formal analysis; funding acquisition; investigation; project administration; resources; supervision. Markus Richter: Conceptualization; funding acquisition; investigation; methodology; project administration; resources; supervision; writing—original draft; writing—review and editing.

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