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Composition analysis of hydrogen-enriched natural gas by high-pressure benchtop NMR spectroscopy with a low-cost flow-through cell design

S.A. Ortiz Restrepo, J. Denninger, M. Adams, R. Thelen, A. Adams *

Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Templergraben 55, 52056, Aachen, Germany

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ABSTRACT

The blending of hydrogen with natural gas (NG) is proposed as the simplest short-term solution for storing, transporting, and using hydrogen. The composition of hydrogen-enriched NG (HENG) blends strongly affects their thermo-physical properties and may influence the mechanical stability of the NG pipelines used. Therefore, its quantification is essential but this is hampered due to the current lack of adequate analytical techniques. Here, we introduce for the first time high-pressure (HP) benchtop proton NMR spectroscopy as a quantitative method for simple and low-cost analysis of pressurized HENG blends. For implementing the method towards an online monitoring scenario, an inexpensive HP flow-through cell, capable of operating up to 245 bar, was designed and tested. The capability of the NMR method was demonstrated on selected blends with different amounts of hydrogen and by in-situ monitoring the change in the composition of a blend with increasing storing time due to the buoyancy of hydrogen.

1. Introduction

Hydrogen (H_2) is known as the lightest, simplest and most abundant element in the universe [1], with a heating value of about 120 MJ/kg at 300 K, which is much higher than the heating value of most fuels (e.g., about 44 MJ/kg for gasoline and 50 MJ/kg for methane at 300 K at 1 atm) [2]. Its high energy density and its potential to be produced from various renewable energy sources endorse its reputation as a clean and efficient energy carrier [3,4]. Therefore, it is anticipated that H_2 will play an important role in different sectors of activities [5]. Globally, the proportion of H_2 energy in the total final energy consumption is expected to increase to about 2% in 2030 and to about 10% in 2050 [6]. Concerning Europe's energy market, it is estimated that the H_2 quota will increase from less than 2% currently up to 24% by 2050 [3] in accordance with the EU's climate-neutral strategic vision.

In spite of its promising future, H_2 faces challenges in terms of production, storage, distribution and utilization [4]. Concerning the main logistic issues, researchers are constantly exploring and developing H_2 storage and transportation technologies in gas, liquid, and solid-state [7]. With the most used approach, H_2 is pressurized at ambient temperature and stored in gas tanks and then transported to its final destination [7]. This approach is however the best suited for shorter distances. Another form of high-pressurized H_2 gas transportation is through dedicated H_2 gas pipelines infrastructure which currently is limited and exists only in few countries [7,8]. Contrary to this, the existing and constantly growing infrastructure for storage and distribution of NG, which consists of a well interconnected pipeline system, is currently considered as an efficient and economical convenient short-term opportunity to store and transport hydrogen-enriched natural gas (HENG) [3,9]. Despite the advantages of this approach, various issues have to be considered because hydrogen has completely different properties than NG. The properties of the HENG blend including density, viscosity, and its flow performance strongly depend on the amount of added hydrogen [10,11]. Furthermore, safety and structural concerns arise with the use of various materials for NG pipelines and pipeline components [7,8,12,13]. The admissible H_2 concentrations for safe operation of NG facilities and of customer appliances are still at the research stage and various investigations report values according to specific applications [8,12]. For instance, studies are currently underway to assess the implications for the entire NG distribution network with H_2 concentrations as high as 50% [7,13,14]. Due to the importance in maintaining the electric grid stability during periods of insufficient wind or solar energy supply, state-of-the-art turbines are undergoing intensive development to operate with HENG containing up to 100% hydrogen [15].

Therefore, a reliable, affordable, and versatile analytical method for

* Corresponding author.
E-mail address: Alina.Adams@itmc.rwth-aachen.de (A. Adams).

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measuring the compositions of HENG blends through the entire transmission and distribution network is in high demand [16,17]. This could potentially help to address and overcome the technological gaps left by the traditional NG metrological devices towards the use of HENG [18].

Gas chromatography (GC) is the gold standard for performing accurate NG composition analysis with low detection limits [19–22]. Such measurements are conducted at a working pressure of 1 atm. For the analysis of HENG samples, GC is equipped with a thermal conductivity detector and helium is commonly used as the carrier gas in the separation column instead of hydrogen [23,24]. Moreover, the use of micro-GC, a compact gas chromatography version, has been demonstrated for online applications including H_2 monitoring with sophisticated sampling accessories needed to be considered depending on the application [24,25].

Concerning optical spectroscopic methods, although the use of infrared (IR) for the composition analysis of NG has already been demonstrated [26], this method fails to measure homonuclear diatomic molecules (e.g., H_2). Raman spectroscopy is another method with high potential for composition analysis of HENG as it can detect H_2 directly and it is able to determine the composition of NG [27]. Recently, drawbacks associated to its sensitivity, spectral background, and artifacts induced by fiber optic systems have been addressed with the development of high-power small-sized lasers and highly sensitive detectors to enhance detection limits [27,28].

High-pressure (HP) NMR spectroscopy has experienced significant developments for the qualitative and quantitative analysis of pressurized gases and supercritical fluids in recent years [29–33]. In particular, high-field HP NMR has been successfully applied to quantify the composition of NG [29] and to directly detect H_2 and quantify its amount [34–36]. But high-field NMR requires dedicated facilities and experienced users. Moreover, it is very expensive in terms of acquisition and maintenance, hampering its implementation for in-field applications. Recently, we have shown that proton HP NMR spectroscopy measurements conducted with a low-cost and small benchtop NMR system can also be successfully applied for the composition analysis of NG up to 200 bar with results in excellent agreement with GC [30,31,37] and to quantitatively monitor the ingress of pressurized hydrogen in green solvents [32] despite a much lower spectral resolution as compared to its high-field counterparts. In addition, benchtop NMR has some more key advantages: it is robust for working in harsh environments found in many industrial applications and it can be even used by non-NMR specialists following a short training period. But despite the capabilities to detect and quantify both the NG and the H_2, both high-field and benchtop low-field NMR have never been applied for the composition quantification of HENG.

A key hardware element for the reported HP NMR measurements are dedicated HP tubes [29–32,37,38]. They have a single opening and are placed inside the NMR spectrometer for conducting the experiments. Yet, the best way to perform a cost- and time-efficient composition analysis of HENG under field conditions would be with the help of flow HP NMR measurements. The most common approach in this case would be to transfer the pressurized gaseous mixture from the pipeline into the NMR spectrometer by a sample loop. The online access provides real-time information about the changes in the composition of the gaseous mixture without the need of sampling, HP tube cleaning, and without time losses while waiting for the results of an analysis conducted in a laboratory. Nowadays, flow NMR is often the method of choice for different applications including reaction monitoring, process control, and industrial screening [39–43] but it fails to be applied under higher pressures ranging from 30 bar up to about 210 bar as encountered in HENG pipelines [8] due to the lack of commercially available HP flow-cells.

Only very few setups are proposed in the literature for conducting flow NMR measurements under pressure conditions higher than 30 bar [44–46]. For instance, an additively manufactured flow-cell working up to 100 bar has been presented [46]. In another study, a flow-cell based on sapphire with two openings operating up to 200 bar is proposed [45]. Yet, due to the sizes of the used caps at both openings, a custom-made radiofrequency coil had to be wound around the sapphire tube which needs to be renewed, tuned, and matched each time when the tube was removed for cleaning purposes making this concept not suited for in-field applications.

In this work we introduce a flow-through cell suitable for HP flow NMR spectroscopy applications at pressures up to 245 bar. It is based on commercially available polyether ether ketone (PEEK) tubing used in high-pressure liquid chromatography (HPLC) applications. In the first step, its spectral performance was investigated in comparison with previous sapphire tube designs suited for benchtop NMR. Subsequently, the experimental reproducibility and long-term stability of the new flow-cell towards NG and respectively H_2 are assessed by conducting measurements at 200 bar for longer periods. Finally, the quantitative composition analysis of a typical natural gas sample mixed with various H_2 concentrations as well as the effect of the storage time are presented as proof of concept for an accurate and low-cost methodology. The whole procedure is amenable to automatization and has the potential to be implemented in in-field investigations. Moreover, we expect that a large variety of applications will benefit greatly from the presented HP flow-through cell concept.

2. Experimental section

2.1. Gas samples

Methane 4.5 (99.995%) and H_2 5.0 (99.999%) gas bottles were purchased from Westfalen AG (Münster, Germany). A binary mixture with a content of 92.43% methane and 7.57% ethane was purchased from Praxair (Ratingen, Germany). Two different types of samples were purchased from Linde AG (Leuna, Germany): 1) a three components gaseous mixture containing 95%, 3%, and 2% of methane (C1), ethane (C2), and propane (C3) respectively, and 2) two samples of diluted hydrocarbons (HCs) in argon, ethane and propane, certified according to DIN EN ISO 6141 (Table SI1).

2.2. Hardware for high-pressure benchtop NMR spectroscopy

The high-pressure setup includes the flow-cell as well as the NMR spectrometer and the computer and fits inside a fume hood (Fig. 1a). Except for the here implemented PEEK flow-cell illustrated in detail in Fig. 1b, the HP setup was previously used with the sapphire-based HP NMR tubes [30–32,37,38]. Although its description can be found in our recent publications, for the sake of reader comprehension, basic details will be specified also here.

The sample gas is initially introduced into a piston-cylinder (Prolight Ti 690-64 MB from Proserv AS, Stavanger), which consists of two physically separated compartments divided by a movable piston. Subsequently, by turning a three-way valve, the sample gas is re-directed into the HP tube or in the case of this paper into the flow-cell. To adjust the pressure on the sample side independently of the filling pressure of the sample gas bottle, nitrogen gas is introduced into the second compartment of the piston-cylinder. Check valves are installed at the gas inlet ports to prevent the pressurized gas from flowing back into the gas bottles to increase the safety measures. Moreover, the piston cylinder serves as a mixing reservoir for generating gas mixtures. For this, the cylinder is initially filled with the first gas sample and then the inlet port is sealed. After that, the second gas is introduced into the piston. The final gas mixture will be then lead into the NMR tube and it is ready for analysis.

2.3. Design of a flow-cell for HP flow NMR spectroscopy up to 245 bar

This work presents a concept of a flow-cell suitable for flow NMR spectroscopy at pressures as high as 245 bar for implementation in

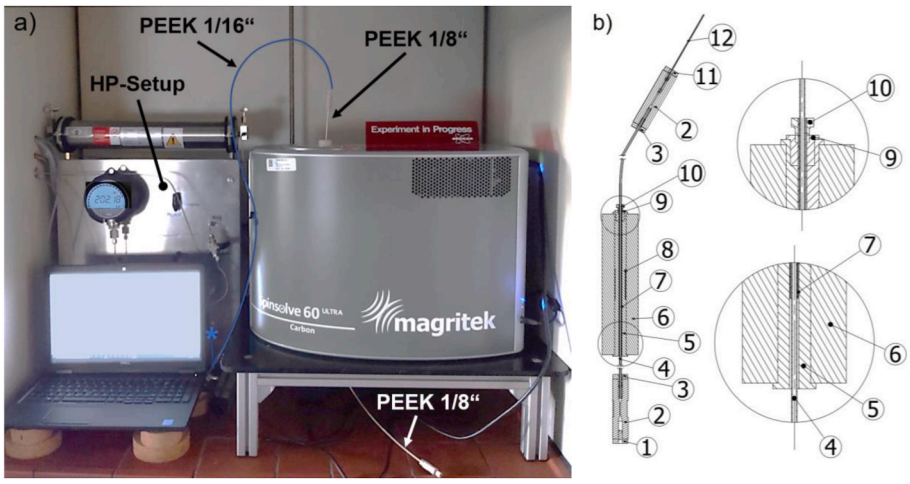

Fig. 1. Photograph of a) HP setup connected to the PEEK flow-cell adapted to the length of a 60 MHz Spinsolve benchtop NMR spectrometer. b) Technical drawing of the implemented PEEK flow-cell: (1) high-pressure PEEK plug; (2) high-pressure PEEK reduction; (3) straight capillary connector 1/8” inner diameter; (4) PEEK flow-cell 1/8” outer diameter; (5) spectrometer bore; (6) spectrometer’s magnets; (7) medium wall NMR tube; (8) radio-frequency coil; (9) spectrometer NMR tube holder; (10) open port cap; (11) finger-tight fitting for 1/16” PEEK tubing; (12) PEEK tube 1/16” outer diameter.

commercially available low-field benchtop NMR equipment. The flow-cell was designed to enable both continuous- and stopped-flow experiments. Among the main constraints to overcome for its usage with the low-field NMR spectrometer were the 5 mm inner diameter (i.d.) of the radio-frequency coil, the length of the magnet bore, and the need of a flow-cell running through the spectrometer with customizable openings to allow manual/automatized sample holding up to 245 bar and its release. Considering this, a very easy plug-and-play like flow-cell based on commercially available PEEK HPLC parts was designed. It consists of multiple connected sub-assembled parts: (a) the flow-cell itself consisting of a PEEK tube with 1/8” outer diameter (o.d.), 0.060” (1.52 mm) i.d., and customizable length (here 50 cm) (Fig. 1b, (4)) rated to work up to 245 bar, (b) a reduction from the 1/8” flow-cell to the 1/16” capillary (Fig. 1b, (2)) consisting of a hex-head 1/8” nut with a replaceable ferrule (Fig. 1b, (3)) and a one-piece finger-tight fitting for the 1/16” PEEK tubing (Fig. 1b, (11)) rated to work up to 344 bar, (c) a second reduction made from a closed 1/16” PEEK plug with a 10–32 thread also rated to work up to 344 bar (Fig. 1b, (1)) for closing the 1/8” PEEK flow-cell after exiting the NMR spectrometer. For the work shown here, both parts (b) and (c) were hand-tightened assembled but they can be easily replaced by parts which can be controlled automatically. All HPLC PEEK components were purchased from VICI Jour (Schenkon, Switzerland). The whole HP setup including the PEEK assembly was checked for leakages with a high-sensitive H_2 detector (Agilent Technologies G3388A) before and during conducting all the measurements presented in this manuscript.

Due to the smaller o.d. of the flow-cell as compared to the 5 mm i.d. of the radio-frequency coil and due to its flexibility, a 5 mm medium wall NMR tube with open bottom (3.4 mm i.d.) (Fig. 1b, (7)) was included to keep the flow-cell straight and centered inside the radio-frequency coil (Fig. 1b, (6)). This is advantageous as it is the region with the highest magnetic field homogeneity within the cylindrical array of the permanent magnets of the NMR spectrometer (Fig. 1b, (6)) [47].

The advantages of implementing accessories based on PEEK are associated to its mechanical, thermal, and chemical stability under a large variety of conditions. For instance, PEEK is commonly found in the existing natural gas infrastructure in components such as couplings, sealing, bearing, or valve systems [48,49]. Unfortunately, only very few studies exist currently about the long-term properties of polymers, including PEEK, in the presence of hydrogen. During accelerated aging hydrogen tests at 80 °C and at 85 bar, PEEK exhibited no changes in its thermal properties but small changes in the surface morphology [50]. More, a very small H_2 uptake over the time of 2 weeks was reported [50]. Given that the experiments were conducted at 80 °C, it is then expected that the uptake at room temperature is much slower and that the morphological changes strongly slowed down [50]. In addition, it is estimated that the morphological changes and the hydrogen uptake will be further reduced due to its lower amount in the blends. PEEK is non-magnetic [51] and because of its low thermal conductivity negligible heat transfer is expected between sample, surroundings, and the NMR magnet which could impact the quality of the NMR results. The proposed flow-cell concept has several key advantages: all parts are commercially available and are inexpensive, the parts (b) and (c) mentioned above can be easily attached by hand, all parts can be replaced independently, and it is very simple and easy to replicate. Moreover, it can be used with any commercially available 5 mm low- and high-field NMR and MRI probe-heads by simply adjusting its length.

2.4. NMR experiments

The proton NMR spectra were collected using a Spinsolve 60 Ultra NMR spectrometer manufactured by Magritek (Aachen, Germany). The spectrometer operates at a proton resonance frequency of 60 MHz and at a temperature of 26.5 °C. Each ^{1}H NMR spectrum used for comparison purposes among the various HP tube designs was acquired with 4 scans. The spectra of the HENG samples with various concentrations of H_2 were recorded with 16 scans. Long-term experiments consist of single-scan ^{1}H NMR spectra acquired for several hours. To maintain the magnetic field homogeneity under unpredictable external room temperature fluctuations, the magnetic field was shimmed every 20 scans as proposed in our previous work [37]. All the experiments were conducted in a stop-flow fashion at 200 bar and started after the gas sample inside the HP tube reached a steady-state. In this way, all gas species inside the tube were fully polarized. The spectra were acquired using 32 k data points and a dwell time of 200 μs. A repetition time of 2 min was used, which exceeds 5 times T_1 of the slowest relaxing component, in our case ethane. Ethane has a relaxation time T_1 of approximately 18 s at 200 bar [31]. The time T_1 of pure hydrogen at 200 bar was measured with the inversion recovery method and had a value of 0.02 s in agreement with reported values in literature [52]. Although T_1 relaxation times of the different species in the mixture change with the mixture composition [36], the use of the repetition time associated with the longest T_1 of the pure component holds also for the mixtures. The time-domain signals were zero-filled to 256k points before applying the Fourier Transformation to enhance spectral resolution in the frequency domain. The phase and baseline of the spectra were automatically corrected by the Spinsolve

software. Further inspection confirmed that no additional processing was necessary. In all investigated mixtures, the methane signal was set at 0 ppm, similar to our previous work [30,31,37].

Prior of measuring a new gas sample, a thorough flushing process was conducted on the piston-cylinder and all HP capillaries including the PEEK flow-cell. Changes in sample pressure are expected to cause fluctuations in sample and magnet temperature leading to broader spectra. Although these effects were minor, a sufficient waiting period was introduced after altering the sample pressure to ensure temperature stabilization and with that improved spectra repeatability. With this new PEEK flow-cell, a time no longer than 30 min was required to achieve steady-state conditions. The magnetic field was then shimmed on each sample to be measured.

3. Results and discussions

3.1. Performance assessment of the flow-cell

In the first step, the spectral characteristics of the flow-cell were investigated. For this, ^{1}H NMR spectra of two gas mixtures measured at 200 bar were used to quantify its performance in comparison with our previous sapphire-based HP tube designs (Fig. 2). For the sake of clarity and to facilitate the comparison, the original sapphire tube design [30, 31], its improved version [32] and the new PEEK flow-cell will be referred as 1st design, 2nd design, and 3rd design respectively.

As one can clearly observe in Fig. 2, the proton NMR spectra recorded using the 3rd design tube have much narrower and more symmetric spectral lines as compared with the spectra recorded with the other HP tubes. For example, in the case of the methane/ethane mixture (Fig. 2a), a decrease in the full width at half maximum (FWHM) of methane of 20% and respectively 14% as compared with the linewidths obtained with the 1st and respectively 2nd design was achieved. The improvements in the linewidth at 0.55% height are even more impressive, with a reduction of 87% and respectively 83% for both peaks when compared to the spectra recorded with the 1st HP tube design and respectively the 2nd HP tube design. Similar improvements were observed also for the methane/propane mixture. In this case, methane and the most prominent peak of the propane multiplets were selected to perform the assessment. The FWHM of both selected peaks exhibited a decrease of about 47% as compared with the older HP tube design. At 0.55% height the methane signal displayed an improvement of 81% in the spectra measured with the 3rd tube design vs the 2nd design. Yet, the comparison of this linewidth for the main propane peak in the spectra recorded with both designs could not be carried out because of the strong overlapping of the multiplets in the spectra recorded with the 2nd design. As demonstrated in our previous work [32], the improvements in linewidth and peak shape achieved with the 2nd design compared to the 1st design are attributed to the avoided surface contamination with paramagnetic particles during the manufacturing process and the improved inner surface quality and thus closer magnetic susceptibility to the values of the gases. Despite the current state-of-the-art design of commercial sapphire cells, the inner tube surface is wavy leading to a non-homogeneous cylindrical distribution of the sample within the sensitive region. The flow-cell proposed in this work is diamagnetic and has a uniform and smooth surface, leading to a better sample distribution in the sensitive volume and with this to improved spectra quality.

The narrower signals obtained with the 3rd design lead to a dramatic increase in spectral resolution such that the complex signals exhibit an improved spectral signature as exemplarily shown for propane (Fig. 2b). Moreover, the signals of the different gas species presented in the mixture are well separated as it can be clearly seen for methane/ethane and methane/propane. The increased signal separation is beneficial as methane is the main component in NG and HENG blends and thus even a small error in its quantification leads to large errors for the other components present in the mixture.

Yet, due to the lowest inner diameter among the three designs, the 3rd design has the lowest amount of sample in the sensitive volume and with this the lowest signal to noise ratio (SNR). The difference in SNRs is quite small compared with the 1st HP tube design but it is larger in comparison with the 2nd HP tube design. While for singlet signals as for methane and ethane, the narrow linewidths partially compensate for the reduction in the signal intensity, a significant reduction of the SNR for the higher order hydrocarbons such as propane is observed (see data in SI). This, however, could be overcome by the increased long-term stability of the measurements such that one could obtain suited SNR during similar period of times as with the other HP tubes. Table SI2 and SI3 in the Supporting Information provide numerical values and differences between the HP tube designs for the peak width and the SNR of the relevant peaks.

A further proof for the improvement of the tube quality was by comparing the NMR results and the certificate values reported by the vendor for a methane-ethane mixture (Fig. 2a). In this case, the composition analysis was done by simple signal integration. The NMR results obtained with the 1st and 2nd HP tube design show a disparity of 0.3 mol% and respectively 0.22 mol% to the vendor values [32], while the disparity went down to just 0.13 mol% with the 3rd HP tube design.

To assess the reliability of the flow-cell concept, the measurement reproducibility and its long-term stability in the presence of pressurized gases were investigated. In our previous work, it was shown that thermal instabilities were detrimental for the linewidth over time and with that for the long-term spectra reproducibility [31,32]. We could recently show that this effect can be removed by a combination of single-scan

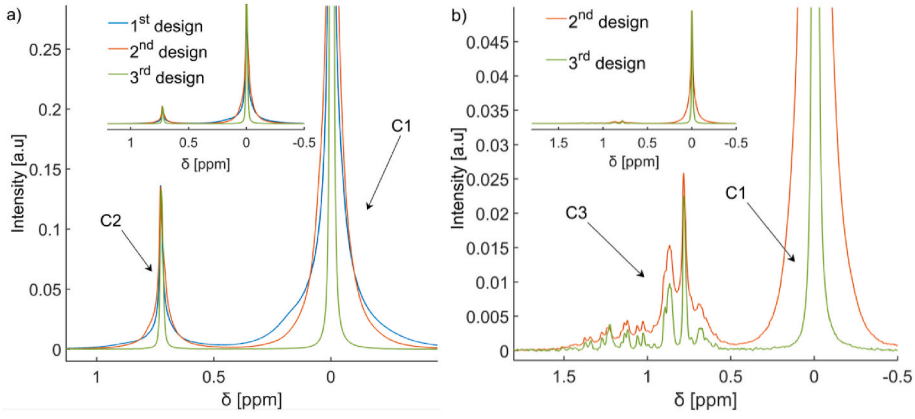

Fig. 2. Proton NMR spectra of two different gaseous mixtures recorded at 200 bar with different HP tubes and 4 scans: (a) methane and ethane and (b) methane and propane. The 3rd design denotes the new flow-cell. The spectra are normalized to the intensity of the methane signal for comparison raisons. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

acquisition, shims after 20 scans to maintain the homogeneity of the magnetic field, and the use of quality control parameters to monitor the spectra reproducibility as long as the temperature variations are not very strong [37]. That is why this approach was also adopted here. Single-scan proton NMR spectra of pure hydrogen and a representative natural gas sample were measured under 200 bar over different periods of time and investigated in term of various spectral properties (Fig. 3). In addition to the quality control parameters proposed in our previous work (total integral and FWHM of the signal of interest), the linewidth at a lower height was also included for an improved characterization of the signal shape. Moreover, the magnet frequency as an indicator of the magnetic field stability was also monitored.

The obtained results are depicted in Fig. 3. For both samples, the total integral was defined as the integral of all peaks available in the recorded ^{1}H NMR spectra. This integral is proportional with the amount of sample present inside the flow-cell and it remains constant over time for both samples. This is thus demonstrating that no gas is lost due to a leakage or diffusion process through the wall of the tube. Additionally, two linewidths measured at two different heights of the main peak in the spectra are used to monitor the changes in the peak shape as it is assumed that their reproducibility over time offer a good description of a reproducible peak shape. Therefore, FWHM was tracked for the H_2 signal and the methane signal of the 3-component mixture for each recorded spectrum. The second linewidth was measured at 10% signal height for methane but at 25% signal height for H_2 due to its broad signal. For both samples, both linewidths showed good reproducibility over time with a larger dispersion shown by hydrogen spectra. This is because the fast spin-spin relaxation time T_2 of hydrogen leads to a broad signal and hence to a lower SNR. The good spectra reproducibility is supported by the stability of the static magnetic field. In conclusion, the data presented in Fig. 3 demonstrates that the novel flow-cell is well suited for measuring both natural gas and hydrogen gaseous samples.

3.2. Quantitative composition analysis of HENG by benchtop ^{1}H NMR

In the next step, the applicability of the novel flow-cell for composition analysis of HENG blends was investigated. For this, two representative and certified NG samples, one containing methane and ethane and one containing methane, ethane, and propane were used as methane, ethane, and propane are the predominant components commonly found in NG samples. The HENG blends were obtained by adding hydrogen to the certified NG sample with amounts determined from the values of the used partial pressures. As a proof of concept, all NMR measurements were conducted at 200 bar. Typical ^{1}H NMR spectra of NG and HENG blends are depicted in Fig. 4a along with the signal assignment. The signal of H_2 is around 4 ppm and well separated from the signals of the NG samples which are in the lower ppm range. This separation will be similar for NG samples containing also higher order hydrocarbons as they give signals in the same ppm range as propane [31]. Moreover, the improvements in the ^{1}H NMR spectra resolution achieved with the flow-cell design leads to an easier recognition of the species present in the mixture. For instance, when comparing the ^{1}H NMR spectra of the gaseous mixtures methane-ethane and methane-propane recorded at 200 bar (Fig. SI1), it can be observed that the peaks of the three components are clearly distinguishable in the spectrum. Moreover, the ethane peak is at a chemical shift where propane, in this case, has negligible signal contribution (Fig. SI1). This remarkable peak separation enables for the first time the quantitative composition analysis of this ternary mixture by simple signal integration (Table SI4), while in recent publications this quantification was only possible by using an advanced analysis approach [29,31,37].

Fig. 4a depicts the ^{1}H NMR spectra of HENG blends containing hydrogen at various relevant industrial concentrations. As expected, the increased hydrogen amount is reflected in higher signal intensity but largely no changes in its position and linewidth were observed. Due to the good signal separation the composition analysis was conducted by using simple signal integration. For a better visualization of the integration limits, the different peak components are highlighted with different colors (Fig. 4a). Since NMR is a quantitative method, the mole fractions of the different species can be calculated by accounting for the number of protons per molecule contributing to the signals in the spectrum. Fig. 4b depicts the excellent agreement between the determined molar composition of the various species in the mixtures using NMR versus the molar composition derived from the partial pressure approach. This good agreement is supported by the fact that the HENG blends were prepared by mixing both samples at low partial pressures [53] at room temperature where the compressibility factor of each component is very close to unity as demonstrated by simulations (Fig. SI2). The obtained compressibility factor for pure H_2 is in agreement with the experimental data reported in Ref. [54], while the compressibility factor of the NG mixture is comparable with the value reported for pure methane in the same reference.

As a further proof of concept for our method, the long-term composition reproducibility of another HENG mixture was investigated by conducting in-situ NMR measurements. The certified NG mixture used here contained methane and ethane. For this, 860 single-

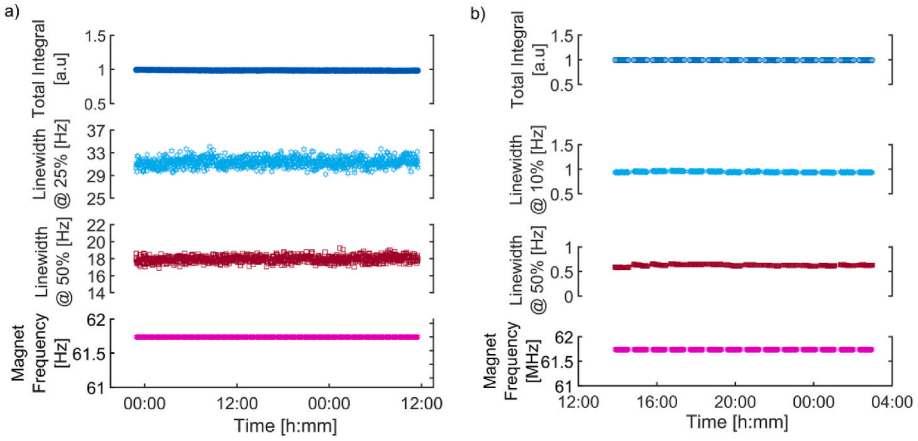

Fig. 3. Long-term stability test of the flow-cell at 200 bar pressurized with: a) pure H_2 over 36 h and b) three-component gaseous mixture containing methane (85 mol%), ethane (10 mol%), and propane (5 mol%) for 12 h. The depicted data give an overview of the change in the total integral, linewidth of hydrogen (a) and methane (b) at different signal heights and the static magnetic field presented in term of frequency with the measuring time. Each point corresponds to the result of a single-scan measurement. The blanks between the data are the shim periods. The data analysis is done automatically using a self-made Matlab script (Version 9.9.0.1570001 (R2020b) Update 4).

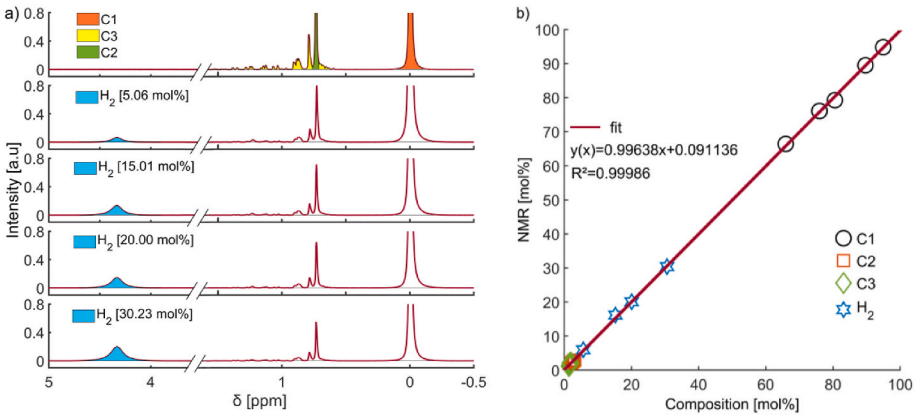

Fig. 4. a) Proton low-field NMR spectra of HENG blends with different amounts of hydrogen recorded at 200 bar. The signals of the components are coded by different colors for easier visual assignment. b) Determined NMR concentrations using the spectra from (a) versus the known/calculated concentrations of the various components in the blends. The linear fit shows an excellent agreement between the two methods. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

scan spectra were recorded at 200 bar over 36 h (Fig. 5) and the determined composition was compared with the vendor values. A change in the signal integrals (Fig. 5a) and with this in the molar concentration of the species (Fig. 5b) within the sensitive volume over time was observed. As the reported linewidths (Fig. 5c and d) and the static magnetic field (Fig. 5e) are largely constant over time, the changes in the composition fail to be attributed to the changes in the stability of the magnetic field or to a leakage. The presence of a leak would be indicated by the results of the highly sensitive H_2 detector used during conducting the measurements. We assign the above observation to an upward migration of H_2 inside the flow-cell towards the piston cylinder located in the upper position due to the buoyancy of hydrogen. The analysis of the data with a linear fit indicates that the change in composition happens with a rate of about 0.19 mol% h^{-1}. The initial molar concentration of the blend was recovered by releasing the pressure of the inert sample side of the piston cylinder and pressurizing it again. The buoyancy effect, causes hydrogen stratification within NG pipelines, making it necessary the use of mixture control devices for its distribution [55]. This phenomenon is of safety concerns associated with the accumulation of H_2 in confined spaces [56,57]. A monitoring in real-time of it, as it can be done easily with our methodology, could help to better characterize it and to optimize the design of NG facilities for the usage with HENG.

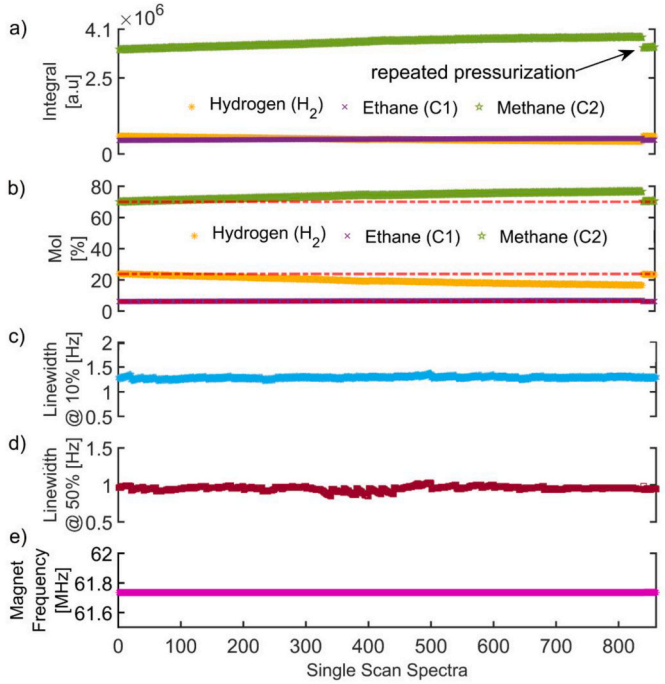

Fig. 5. Long-term in-situ composition monitoring of a three-component gaseous mixture with methane (68 mol%), ethane (6 mol%), and hydrogen (26 mol%) using the flow-cell tube design at a pressure of 200 bar over 36 h by recording single-scan spectra. Each spectrum required about 2 min measuring time. Signal integrals of methane, ethane, and hydrogen; (b) the composition of the mixture inside the NMR sensitive volume; (c) linewidth of methane at 10% height; (d) linewidth of methane at 50% height; and (e) static magnetic field presented in term of frequency versus the measuring time. The red dashed lines in (b) serve as a visual guide and denote the calculated composition using the known composition of the methane-ethane mixture and the used partial pressure for preparing the mixture with hydrogen. The data analysis was done automatically using the Matlab script. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

While the above presented results were obtained by conducting NMR measurements in a manual "stop-flow" fashion, the proposed flow-cell can be adapted easily to perform automatically stop-flow and continuous-flow data sampling. However, due to the low concentrations of the higher-order hydrocarbons in NG, we envisage that online measurements in stop-flow would be more advantageous rather than in continuous-flow. Moreover, as shown by the data presented in Figs. 2 and 5 and in our previous publication for NG mixtures [37], the experimental procedure including the data acquisition and composition calculation can be done automatically.

4. Conclusion

This work reports for the first time a methodology for a reliable and cost-efficient quantitative composition analysis of HENG. It makes use of high-pressure proton NMR spectroscopy conducted with a low-cost and small benchtop NMR spectrometer. It takes advantage of a concept for a flow through-cell suited to conduct flow NMR measurements at pressures up to 245 bar. The design of the flow-cell is simple, inexpensive, and easy to replicate. It does not need any special skills or facility requirements and therefore opens up new avenues also for scientists and applications outside the NMR community. The flow-cell shows strong improvements in the quality of the spectral signatures as compared with HP tubes designs previously used for measuring pressurized gaseous mixtures. Moreover, it presents long-term stability in the presence of NG and pure hydrogen.

The experimentally determined compositions of HENG blends with variable quantity of hydrogen are in excellent agreement with the compositions determined by using the partial pressure approach in a

pressure and temperature regime where the theoretically determined compressibility factor is close to unity. Furthermore, as the NMR method is sensitive to even small changes in the composition, the buoyancy of hydrogen in a relevant HENG blend was monitored in-situ and the speed of changes determined.

The introduced NMR methodology represents a step forward towards online composition analysis of HENG blends under in-field conditions. The knowledge about their composition and the associated temporary changes is of key importance for ensuring the safety of the used infrastructure and for enhancing the decision-making process along the entire existing natural gas network. The first steps for automated data acquisition and analysis are already implemented and used during this work. All the other necessary steps to obtain a fully automated method are currently under development in our laboratory.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

S.A. Ortiz Restrepo: Data curation, Formal analysis, Investigation, Methodology, Writing – original draft. **J. Denninger:** Data curation, Investigation, Methodology, Writing – review & editing. **M. Adams:** Conceptualization, Investigation, Methodology, Writing – review & editing. **R. Thelen:** Conceptualization, Investigation. **A. Adams:** Conceptualization, Funding acquisition, Methodology, Project administration, Supervision, Writing – review & editing.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2024.04.119.

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