In-situ neutron imaging of hydrogenous fuels in combustion generated porous carbons under dynamic and steady state pressure conditions

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Abstract

We report results from experiments where we characterize the surface properties of soot particles interacting with high-pressure methane. We find considerable differences in behavior of the soot material between static and dynamic pressure conditions that can be explained by multiscale correlations in the dynamics, from the micro to macro of the porous fractal-like carbon matrix. The measurements were possible utilizing cold neutron imaging of methane mixed with combustion generated carbon (soot) inside steel cells. The studies were performed under static and dynamic pressure conditions in the range 10-90 bar, and are of interest for applications of energy storage of hydrogenous fuels. The very high cross sections for neutrons compared to hard X-ray photons, enabled us to find considerable amounts of native hydrogen in the soot and to see and quantify the presence of hydrogen atoms in the carbon soot matrix under different pressure conditions. This work lays the base for more detailed in-situ investigations on the interaction of porous carbon materials with hydrogen in practical environments for hydrogen and methane storage.

Key Words: In-situ measurements, high pressure, Soot, adsorption, methane, neutron radiography, pressure.

1 Introduction

Energy consumption for transportation, heat, household power, and manufacturing is globally increasing. This implies strongly raised levels of pollution and risks to the environment and human health. Emission control will continue to be more stringent and require strategic solutions to improve combustion processes causing less pollution and higher fuel efficiency. Hydrogen is one of the purest forms of energy virtually causing no pollution. It is richly available in water, methane and natural gas and can also be extracted from biomass. Methane is a carbon containing gaseous fuel with the highest hydrogen to carbon ratio (H/C) and is readily available and easy to produce. However, energy storage requires gas to be compressed to high pressures in order to achieve sufficient energy capacity in e.g. fuel tanks for transportation. Recently, considerable attention has been directed towards carbon based materials (see [1] and references therein) for energy storage at reduced pressures.

Different carbon structures can be produced from combustion-like processes, such as fullerenes, nanotubes, and graphite. These may be found as components [2-5] in carbon soot, one of the most common unwanted by-products from incomplete combustion, which normally has a negative effect on health and the environment. It can also have positive aspects in that it may play an important role for clean energy conversion in combustion due to its material properties such as low density and fractal structure. In connection to our investigations on ethylene atmospheric pressure flames and soot condensation on metal plates utilizing in-situ X-ray scattering diagnostics [6-9], we obtained fractal-like (carbon) low-density soot materials (below 100 mg cm^{-3}) [6,7]. This material showed considerable “thermal elasticity” with a density that changed by 30% between 300 and 600 K, approximately. We have also observed that flames can produce graphene/sheet-like structures either in few layers [10] or as components in the soot particles [11]. These structures are characterized by a high surface-to mass ratio, and in principle, the surface properties of the nanostructure subunits of soot particles can be changed by preparation utilizing controlled

oxidation processes. In addition, one can mix different materials in order to obtain improved overall absorbent properties, which can be difficult to estimate without any experimental investigations. These should preferentially be done in-situ under conditions as close as possible to real and operative conditions for fuel tanks.

Although hard X-rays have been used to characterize soot structure in flames (see e.g. [11] and references therein), it is relatively difficult to evidence the contribution from hydrogen, due to its low cross section. In addition, many of the electron microscopy techniques also have a problem with identifying hydrogen in samples. This fact makes it hard to study the hydrogen in materials, in particular if the containers are made out of stainless steel, which X-rays have difficulty to penetrate. In comparison, neutrons have a large attenuation cross section for hydrogen atoms (the largest among the present species) and relatively low cross sections for carbon and metallic species. Thus neutrons are essential to study the dynamics of hydrogenous substances in various challenging environments, such as, in tanks [12], engines and combustors during very close to real operation conditions.

This work presents a method for in-situ investigations on the interaction between porous carbon materials and hydrogenous substances in pressurized steel containers utilizing cold neutron radiography. Neutron radiography was chosen before scattering techniques [13-15], which have proven to be of great value to study interactions on the micropore scale (diameter smaller than 2 nm). In our view radiography gives a more robust and faster ways to perform experiments and acquire and analyze data on complex material systems, although at the cost of loss of spatial resolution on the nanoscale. We report results from measurements under dynamic and static pressure conditions on combustion soot and methane, which is a hydrogenous gas of commercial interest for clean energy utilization. To simplify the reading of this work we have in Table 1 summarized the abbreviations and symbols that are used throughout the text.

2 Experiments and results

The experiments were performed at the High-Flux Isotope Reactor (HFIR), beamline CG-1D [16, 17] at the Oak Ridge National Laboratory (ORNL). Fig. 1 shows an overview of the basic elements of the set-up. The neutron radiography detector, which can partially be seen in Fig.1a (Al window behind the cell), consists of a $^6\text{LiF-ZnS}$ scintillator with a charge coupled device (CCD) camera described in [17]. The neutron flux of the polychromatic beam with a peak neutron wavelength of $2.6 \text{ \AA}$ was on the order of $5 \times 10^6 \text{ n s}^{-1} \text{ cm}^2$ at the sample position. The collimation factor was $L/d = 5650/11$, i.e., 514. L and d are the flight tube length and the aperture width, respectively. The neutron beam travels inside an Al tube filled with He gas to minimize air scatter before reaching the cell made of stainless steel (Swagelok cross) described in Fig. 1 a, containing the sample (with soot) and reference (empty) containers, (L) and (R), respectively. These were cylindrically shaped and had an inner diameter of 16 mm. The transmitted beam was then measured by the CCD detector, with a resolution of $100 \text{ }\mu\text{m}$ and an exposure time of 50 s. The recorded images were then analyzed using ImageJ [18]. The red wide arrows in Fig.1a show the neutron passages related to the main analyzed transmission regions through the sample and reference cells. These containers were perforated to enable flux and pressure equilibration of gas inside the entire cell system. As the gas was introduced into the cell system the two containers were filled with gas at the same pressure but (L) had less space of gas due to the presence of the soot. Examples of radiographs of the cross are shown in Fig. 1 b, and c, together with an image, Fig. 1d, showing the presence of methane obtained from information in b and c. The regions of interest for (L) and (R) are marked by red boxes in Fig.1 b - d. The pixels counts were averaged by 30×30 pixels and then evaluated over 28×28 pixels, which corresponded to a real object area (OA) of $1 \times 1 \text{ mm}^2$. We calculated that the neutron path length inside the cells did not vary more than $65 \text{ }\mu\text{m}$ over the entire OA, yielding less than 0.4% in variation of the path length and thus is below the limit of resolution of the experiments.

The cell system included a transducer (Ellison Scientific International, ESI) that measured the pressure and temperature with a temporal resolution of 0.1 s, which enabled us to assign cell pressures to each recorded image.

2.1 Characterization of the soot material

The soot material was obtained by condensation of particles onto a steel plate in an ethylene diffusion flame according to the processes described in [6,7]. It was removed from the plate and stored for 7 years under atmospheric conditions. This sample will be referred to as the “original” sample in the following text. Figure 2 shows high-resolution transmission electron microscopy (HRTEM) images of the material measured after the experiments. It contained two groups of particles: (1) primary particles with a narrow size distribution of about 20 nm diameter with mainly turbo-stratic structure, and (2) larger more amorphous particles. Pictures (a) to (c) show a sequence of gradually zoomed measurements of the same probed soot region. (d) and (e) are examples from similar regions, where brighter very localized areas appear more distinctly and should indicate inner voids formed during the aggregation of sub-primary particles into primary particles that was evidenced from in-situ X-ray scattering measurements (see [6]) on the same flames used to produce the investigated sample. These pores are probably isolated from the gas phase and are in the micro-pore ($D < 2$ nm) region (IUPAC definition). Furthermore, they seem to be more weighted to the ultra-micro-pore ($D < 0.7$ nm) than the super-micro-pore size region ($D > 0.7$ nm).

More importantly, in the same size region, we can also find other structures on the surfaces of the primary particles that are accessible to the gas phase and thus potentially play a role in the absorption process of methane. We find strand-like or micro-sheet-like structures (most probably with strong sp^2 character) that partially stick out of the surface, that have considerable orientation along to the surface of the primary particles, i.e., “tangential”, that we refer to as “nano-pockets”. These may be relatively flexible and not completely bound and have a loose end through which methane molecules can penetrate. These

flat like pores appear to be in the ultra-micro-pore size region in thickness and can reach the super-micro-pore in depth. Some of these structures can also be more “radially” oriented and probably have flat, but less flexible properties and confined to the ultra-micro-pore region (see upper circle in Fig. (d)). In Fig. 2 (f) we find that some primary particles can adhere, forming voids that can be slightly larger than micro-pores. We have also labeled them as nano-pockets, however, they are of a different nature than the ones discussed above, and we cannot yet determine if they are accessible to the gas phase, although the images show relatively thin walls. In terms of IUPAC definitions the meso-pore ($2\text{ nm} < D < 50\text{ nm}$) and macro-pore ($D > 50\text{ nm}$) scales have a different meaning for these fractal particle based systems, in that they are more related to the properties of the interstitial space or “free” volume of the soot matrix, which therefore depends on the level of compression of the material. These are therefore more flexible than micro-pores and can be externally/mechanically controlled. In Fig. 2 (a) and (f) we have marked a couple of 2-D projections of “open” structures in the soot material that are in the meso- and macro scales.

Besides pore-related structures that can be evidenced from HRTEM, surface polar, oxygen containing groups can have important attractive properties for adsorption of methane on the particles’ surfaces. Investigations by other groups have shown that they can play an important role for surface adsorption. For instance, from infrared studies at 173 K utilizing silica (quartz) and alumina, which contain oxygen groups on the surface, one research group found that the C-H vibrational of methane shifted to lower energies as a result of bonding to the surface, most probably due to surface distributed –OH since their frequencies also were shifted lower [19,20]. In addition, quantum chemistry density functional theory applied to surface molecules of anthracite in coal has shown that methane is preferentially absorbed in the hydroxyl-containing side of the side chain, but less favorably at the position of the benzene ring [21].

In our case, X-ray photon spectroscopy (XPS) measurements were used to characterize the soot material’s chemical surface, which was found to be composed of 93% carbon and 7% oxygen. The carbon

was mostly sp^2 with some sp^3 , as confirmed by Raman scattering measurements. The XPS could in more detail quantify the bonding of oxygen as 2.2% C=O, 1.3% O-C=O, 3.8 % C-O, and 0.4% H₂O. These chemical groups agreed with signatures found from synchrotron Fourier transform infrared transmission microscopy (FT-IR-TM) measurements on a sample from the same batch that was unexposed to neutron radiation (see Fig.3). The considerable agreement found between bulk sensitive measurements based on particle transmission such as FT-IR-TM and the surface sensitive XPS on similar samples suggest that the carbon to oxygen ratio was rather similar on the inside and outside (surface) of the primary particles. Agreement was also found with bulk measurements utilizing energy dispersive X-ray spectroscopy (EDX) performed on a fresh soot sample obtained from another diffusion flame. These facts suggest that the particle precursors working as building blocks of the primary particles show similar atomic composition consisting of partially oxygenated chemical species. To summarize the above, Table 2 shows the main features of the soot divided into three classes that are related to pore and chemical properties.

In order to determine the native hydrogen content of the soot particles neutron attenuation measurements were performed. From Table 3 we find that the attenuation cross section for the cold neutrons (wavelength 2.6 Å) used in our experiments is between 14-15 times larger for hydrogen than for carbon. Since X-ray attenuation is weaker for hydrogen than for carbon (for 10 keV radiation it is about 73 times), hydrogen detection can thus be three orders of magnitude more sensitive utilizing cold neutrons instead of hard X-rays. In practice, neutrons would be able to detect pressurized gaseous hydrogen surrounding carbon nanoparticles and thus be well-suited for the study of the interaction hydrogen and methane with carbon nanoparticle assemblies such as soot, the structure of which can be characterized by X-ray scattering techniques (see [5-7,9,11] and references therein).

2.1.1 Quantifying native hydrogen in the soot sample

In this section we give a summary on a method to determine the mole fraction of hydrogen and the total amount of atoms in a soot sample by combining XPS or EDX and neutron attenuation measurements. For example, EDX or XPS can be used to determine the relative C- and O-atom content in the volume resp. surface of the material's soot particles, in practice excluding hydrogen. The information on hydrogen is instead obtained from independent neutron attenuation measurements, which contain information on the relative H-, C-, and O- composition.

The relation between sample mass mole fractions of atomic species can be expressed as

$$m = x_H \times n \times M_H + x_C \times n \times M_C + x_O \times n \times M_O \quad (1)$$

where n is the total number of moles of atoms in the sample. x_H , x_C , x_O , and M_H , M_C , and M_O are the mole fractions and molar masses of hydrogen, carbon, and oxygen, respectively. From XPS and/or EDX one gets the mole fractions r_C and r_O , where, $r_C + r_O = 1$. Hydrogen (H), i.e., r_H , has not been included because the sensitivity of the mentioned techniques to this species is very low compare to C and O.

In order to evaluate the H-content neutron transmission measurement one can perform measurements with helium gas (typically, 3-5 bar), which shows very weak attenuation. The following equations for the mass and absorbance can then be applied.

$$m = n \times [a_1 + a_2 \times x_H] \quad (2)$$

$$A = c \times n \times [a_3 + a_4 \times x_H] \quad (3)$$

where the variables a_1 - a_4 , and c are defined as

$$a_1 = r_C \times M_C + r_O \times M_O \quad (4)$$

$$a_2 = M_H - a_1 \quad (5)$$

$$a_3 = r_C \times \sigma_C + r_O \times \sigma_O \quad (6)$$

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$$a_4 = M_H - a_3 \quad (7)$$

$$c = D \times N_A / V_c \quad (8)$$

where D , V_c , are the diameter and volume of the sample cell in our experiments, respectively, and N_A is Avogadro's number. The following explicit expressions for x_H and n are then obtained:

$$x_H = \left[\frac{c \times m \times a_3}{A} - a_1 \right] / \left[a_2 - \frac{c \times m \times a_4}{A} \right] \quad (9)$$

$$n = \frac{A}{c \times [a_3 + a_4 \times x_H]} \quad (10)$$

In the beginning before realizing the significance of hydrogen in the soot, we only considered carbon. The value of n could then be found from Eq. (10) setting $x_H = 0$ and $x_O = 0$ in Eq. (6) and the mass, m , by Eqs. (2) and (4) setting $r_O = 0$, without weighing the sample. In a second set of experiments, (the results of which will be presented in another communication) we weighed and used the fresh sample referred to in the previous section 2.1 before the neutron absorbance measurements. We found that the value of m obtained from considering only carbon was three times higher than that weighed for the fresh sample utilizing the same volume and diameter specifications on the sample cells. Due to the similarities of the original and fresh samples in terms of chemical composition, the mass of the original sample, m , was therefore retrieved from a combination of absorbance measurements on both samples, yielding, A and A_{fresh} , respectively, and the weight, m_{fresh} on the fresh sample. The resulting mass of the original sample was then given by $m = A \times m_{fresh} / A_{fresh}$.

With $r_C = 0.93$ and $r_O = 0.07$ from XPS, $A = 0.1511$ from neutron attenuation, we obtain the corrected value for the original sample, $m = 0.1635$ g, from the method above and $x_H = 0.14$, $x_C = 0.80$, $x_O = 0.06$, and $n = 1.53 \times 10^{-2}$ mol. Calculations show that x_H is relatively insensitive to the oxygen concentration compared to that of carbon, since their cross sections are relatively similar (see Table 3). As an example,

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$x_H = 0.14$ was also obtained for the fresh sample when r_O (obtained from EDX) varied between 0.01 to 0.09.

2.2 Characterizing the soot material's interaction with methane

In order to characterize the interaction of the carbon soot with the methane gas quantitatively, we first need to specify some fundamental equations utilized for the evaluation of the experimental data.

The transmitted neutron beam flux, I , i.e., number of neutrons per area and time units can be expressed by the Lambert Beer law according to eq. (11). I_0 is the flux of the incident beam on the cell, a_{cell} is the attenuation due to the cell material, μ is the linear attenuation coefficient in cm^{-1} and D is the sample thickness and diameters in cm of the sample and reference cells. N is the number concentration per unit volume in cm^{-3} , σ the total cross section in cm^2 , and β is the attenuation coefficient per unit pressure and length for a gas in $\text{bar}^{-1} \text{cm}^{-1}$ and p is in bar.

$$I = I_0 \times a_{cell} \times \exp(-\mu \times D) = I_0 \times \exp(-\sigma \times N \times D) = I_0 \times \exp(-\beta \times p \times D) \quad (11)$$

In practice one gets the following expressions for (L) and (R):

$$I_L = I_0 \times a_{cell,L} \times \exp\left(-\left[\sum_j \sigma_j \times N_j \times D\right]_{soot}\right) \times \exp(-\sigma_{gas} \times N_{gas} \times D) = I_0 \times \exp\left(-\left[\sum_j \sigma_j \times N_j \times D\right]_{soot}\right) \times \exp(-\beta_L \times p \times D) \quad (11a)$$

$$I_R = I_0 \times a_{cell,R} \times \exp(-\sigma_{gas} \times N_{gas} \times D) = I_0 \times \exp(-\beta_R \times p \times D) \quad (11b)$$

In our applications $a_{cell,L} = a_{cell,R}$. We define the absorbance due to the gas species in (L) and (R) as A_L and A_R , respectively as given in Eq. (12a) and (12b) below. The fact that helium has a low cross section (see Table 3) and yields hardly any measurable attenuation for the conditions of the experiments gives the

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possibility to express the absorbance due to methane by utilizing Eq. (11a): By dividing the values of I_L for helium, $I_{L,He}$ (Helium at 3-5 bar) with that for methane, $I_{L,Me}$, one obtains the ratio $\gamma_L = I_{L,He} / I_{L,Me}$ and $A_L = \ln(\gamma_L)$. The corresponding procedure is then repeated to get A_R . As a control on helium attenuation, calculations show that for 5 bar helium at 296 K and for $D = 1.6$ cm A_R in Eq. (12b) yields 2.65×10^{-4} , i.e., a negligible number for our investigation on methane attenuation.

$$A_L = \beta_L \times p \times D \quad (12a)$$

$$A_R = \beta_R \times p \times D \quad (12b)$$

The set-up gives the possibilities to measure the cross section of a gas in the reference cell. Assuming it obeys the perfect gas law it can be evaluated from the absorbance measurements using equation (13), where R is the gas constant, T the absolute temperature and N_A is Avogadro's number. The factor 10 in the equation is taking into account the relation between SI units and the cm and bar units used for length and pressure, respectively. R is defined as $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

$$\sigma_{att} = \sigma_{gas} = (10 \times \beta \times R \times T / N_A) \quad (13)$$

The absorbance of the soot sample, A_{soot} , in (L) can be obtained utilizing Eq. (14a)

$$A_{soot} = \ln \left(\frac{I_{R,He}}{I_{L,He}} \right) \quad (14a)$$

Utilizing the method described in section 2.1.1, we can for hydrogen, carbon, and oxygen species, individualized by index j in Eq. (14b), obtain their number concentrations through the expression

$$A_{soot} = \left[\sum_j \sigma_j \times N_j \times D \right]_{soot} \quad (14b)$$

where σ_j are the cross sections given in Table 3.

The practical procedure of data evaluation was sequenced in the following way: (1) First, the images were compensated for background and then normalized against the open beam images (see Fig. 1 b and c). This was done for both cases of helium and methane; (2) The resulting images of the two gases were then divided (pixel by pixel) with each other (see Fig.1 d) to yield images of the ratio of counts, γ , (background compensated); and (3) A_L and A_R for the respective red marked OA regions of (L) and (R) in Fig.1 d were obtained for different pressures of methane, p_{Me} , utilizing Eqs. (15) and (16), which also include expressions containing the attenuation coefficients for (L) and (R), $\beta_{Me,L}$ and $\beta_{Me,R}$, respectively.

$$A_L = \ln(\gamma_L(p_{Me})) = \beta_{Me,L} \times p_{Me} \times D \quad (15)$$

$$A_R = \ln(\gamma_R(p_{Me})) = \beta_{Me,R} \times p_{Me} \times D \quad (16)$$

In general, $\beta_{Me,R}$ is supposed to be constant, whereas $\beta_{Me,L}$ is expected to increase if there is any adsorption/absorption on the soot material. Throughout the present pressure range, however, the methane attenuation coefficient of the soot filled cell in our experiments was smaller than for the empty cell, because soot reduces the free volume available for the gas. At higher pressures, one may expect that the attenuation (and the methane content) of the soot filled cell exceeds the empty cell.

Two different cases were studied: (A) Gradual pressure release and (B) Quasi-static steady state stepping up pressure. The results are summarized in Fig.4. From Fig. 4 one notices that for (A) the absorbance for (R) and (L) are considerably proportional to the pressure p of the cell system. The data points given by “88ln(γ_R)” and “94ln(γ_L)” represent these quantities scaled by the constants 88 and 94, respectively, to fit the pressure decay curve after ~ 9650 sec. Before that time point, i.e., under the more static conditions “94ln(γ_L)” shows values noticeably higher than that of the pressure. This fact becomes

more evident in Fig. 4 b where the difference absorbance, $A_{Me,R} - A_{Me,L}$, is plotted for both conditions (A) and (B). For (A) there is an almost linear dependence of $A_{Me,R} - A_{Me,L}$ as a function of pressure up to approximately 33 bar. This increase with pressure is stronger than for (B). Between 30 and 50 bar the value increased less and approached the values for the steady state (B). This can partially be explained by the release dynamics in (A) that started from a steady state condition (similar to (B)) at 50 bar before the pressure decreased. The data points for $p = 0$ bar in Fig. 4 b and c are the values for a cell empty and free from methane and is not an experimental, but theoretical or expected data point. The temperature measured by the transducer during the experiments was considerably constant $295.9 \pm 0.1(1\sigma)$ K. The steady state condition (B) showed an almost perfect linear relation with pressure, with as slope of $9.39 \times 10^{-5} \text{ bar}^{-1}$ in the entire range up to 90 bar. $A_{Me,R}$ in Fig. 4 c, i.e., the absorbance for the reference cell under condition (B) shows a considerably linear dependence on pressure. Linear regression yields a coefficient (corresponding to $\beta_{Me,R} \times D$) of 0.01197 and a standard error of 8.1×10^{-5} , implying that the steady state condition for methane in (R) obeys the Lambert-Beer law. Utilizing Eq. (13) we obtained $\sigma_{att} = \sigma_{Me} = 300 \text{ barn}$, which is about 11 % lower than expected 336 barns from theory given in Table 3. In order to get a more exact evaluation of the cross section, the energy distribution of the neutron beam and the spectral sensitivity of the detector have to be taken into account. The cross section in Table 3 are given for the peak wavelength 2.6 Å.

The Degree of Filling of Methane (*DFM*) in (L) is defined in Eq. (17) and is reported in Fig. 4 d for different methane pressures.

$$DFM = A_L / A_R = \frac{\beta_{Me,L}}{\beta_{Me,R}} \quad (17)$$

Data showed differences in the behavior of *DFM* vs pressure between cases (A) and (B): (A) presented lower values than (B) as the pressure was lowered. These are effects seen for both the difference absorption and the *DFM*. We cannot yet give a clear answer to the different behaviors of (A) and (B), but suggestions are given in the discussion of section 3.

Analysis of the steady state conditions (B) given in Fig.4d suggests that there was a slight decrease of *DFM* with pressure based on linear regression analysis. In order to get a first level interpretation of the results we set a “model” based on the amount of methane molecules than can cover the surface of the soot particles in the material according to the procedure described in Fig.5. The soot surface, A_s , was calculated with the approximate assumption that the soot consisted of spherical carbon primary particles with the density 2 g cm^{-3} [23-25] and diameters of 20 nm. From the helium transmission measurements, (yielding negligible gas attenuation as shown above) we obtained the amount of carbon atoms in (L). Utilizing the attenuation coefficient for the carbon atom at the peak neutron wavelength, we determined the soot volume fraction (*SVF*) and the free volume fraction ($FVF = 1 - SVF$). The next step was to assume that A_s would be covered by methane molecules with a certain probability, defined by the relation $\eta = a + b \times p + O(p^2)$, where p is the pressure in bar and a and b are parameters representing a pressure independent (long-range) and b a linearly pressure dependent (short range) part, respectively. $O(p^2)$ is a non-linear term, that can be related to effects of condensation in the interstitial volume of the soot matrix and non-linear accumulation in pores, which are summarized in Table 2.

The total number of primary particles, N_p , and their total surface $A_s = N_p \times A_p$, where A_p is the the average surface of the primary particle were then determined. In this approximation we used that there was no “necking” formed between the touching primary particles. Calculations followed on establishing the total number of methane molecules, N_{mso} , that could cover the total surface of the soot sample, A_s , primarily assuming a rectangular symmetry of surface distribution (α) of methane molecules, and

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secondly, a hexagonal distribution (β), which yields and increased number by approximately 15%. The resulting number of methane molecules adsorbed/absorbed by the soot, N_{ms} , and the corresponding expression for DFM then became:

$$N_{ms} = N_{ms0} \times \eta = N_{ms0} \times (a + b \times p) \quad (18)$$

$$DFM = (N_{ms} + N_{mf}) \left/ \left(V_c \times N_A \times \frac{p \times 1.000 \times 10^5}{R \times T} \right) \right. \quad (19)$$

where N_{mf} was the number of methane molecules in the (Interstitial) free space ($FVF \times V_c$) of the soot matrix, where V_c was the cylinder volume of (L), equal to that of (R) in our case. N_A is Avogadro's number, R the gas constant and T the absolute temperature. In Eq. (18) the higher order terms, $O(p^2)$, were not included since we did not find any significant changes of DFM with pressure in the high pressure regime during step-up. Other motivations for this choice were given by the low density of the soot material, the relatively large characteristic interstitial volume and the observed linear dependence of the absorbance of methane with pressure for the reference cell.

In Fig. 4 d we have given the best fit of DFM for $D_p = 20$ nm in case (B) that yields $a = 2.5 \times 10^{-4}$ and $b = 7.47 \times 10^{-3} \text{ bar}^{-1}$, respectively. Results from fits using different choices of particle diameters showed both constants to be proportional to the diameter. Therefore, the parameter $g = a / b$, equal to 0.033 bar for this fit, would be preferred to describe the relation between of the long- and short-range interactions.

The model shows that DFM decreases with the increase of pressure when long range-surface mediated forces are dominating. This is due to the fact that the amount of surface bound- (correlated to the coefficient a) compared to free gas-methane decreases with pressure. In the analysis described in Fig.4 we assumed primary particles with the density 2 g cm^{-3} [23-25] of mainly carbon atoms that may not be the best choice for the analysis. Presence of strongly neutron attenuating native hydrogen in the soot may yield a considerably higher FVF than reported in Fig.4 d. An increase of resulting FVF might be partially

compensated by a lowering of the primary particle mass density with the presence of native hydrogen. This is a question that is discussed in the following section and that has to be answered in follow-up studies.

3 Discussions

In order to determine $FVF = 1 - SVF$, the densities, ρ_p , of the primary particle have to be given. To begin with, we can make estimates for different conditions. One is to assume the condition $b = 0$ in Eq. (18), e.g., for the case with very few microspores or small meso-pores valid for “flat” or “slippery” particle surfaces, which would be relatively close to the conditions found from the HRTEM results. At the high pressure end (below the limit of non-linearity where $O(p^2)$ sets in) the *DFM* should yield a value close to that of the *FVF*. Another condition is to consider the low limit *DFM* of the gradual release case. It is approached in the low pressure limit and it may indicate that the *FVF* decreases as the pressure is gradually released causing the soot material to compress in the observed volume, but more studies will be required to verify this hypothesis. In particular, the continued application of neutron radiography to observe heterogeneous soot densities may have tremendous value. In Fig. 6 and Table 4 we show how the *a*- and *b*-coefficients affect the calculated *DFM* for $\rho_p = 2.0 \text{ g cm}^{-3}$ (conditions A-F, only carbon assumed in the primary particles) for different theoretical fits. We also show how ρ_p and *FVF* relate to the *a*- and *b*-coefficients fit the steady state *DFM* for the atomic species composition derived from the procedure described in section 2.1.1 based on sample mass and neutron absorbance measurements. For condition G, we assume $b = 0$, e.g., “pore-less” primary particle surfaces and get $\rho_p = 1.37 \text{ g cm}^{-3}$ and $FVF = 0.926$, which is the upper pressure limit of the steady state *DFM*. This density value is not far from that reported by another group [26] as fits of experimental data on the effective density vs. aerodynamic diameter for fullerene soot. They obtained for our primary particle size ranges 1.36 g cm^{-3} for 40 nm, and 1.67 g cm^{-3} for 20 nm aerodynamic diameters. For the case of the condition H we take into account the lower value

for the gradual release experiment, $DFM = 0.894$, and obtain $\rho_p = 0.96 \text{ g cm}^{-3}$. Both G and H yield very similar fits to case A reported in Fig.6 a. These density values are much lower than from our specified literature references [23-25], and could be due to less mature soot particles. Particle mass density appears to be an important parameter in soot formation modeling and values between 1.0 and 1.8 g cm^{-3} have been suggested [27]. Studies on diesel soot [28] have shown that the densities of the particles tend to decrease from approximately 1.8 g cm^{-3} as they get smaller below 100 nm . This was ascribed to an increased contribution from organic carbon (OC) with 0.8 g cm^{-3} consisting mainly of lubrication oil. Although the major component of OC was ascribed to lubrication oil in the engine in that study, heavier molecular components formed in the flame gas during soot formation may play a similar role in our diffusion flames.

In order to get an independent estimate of ρ_p , we had the skeletal density measured by the helium pycnometry technique (see e.g [29,30] for examples given by other groups) yielding averages below 1.4 g cm^{-3} . For $\rho_p = 1.34$, from one of the pycnometry results, the model described in this work yields coefficient $b = 4.00 \times 10^{-4}$, $a/b = 0.625$ (the a -coefficient used was 2.50×10^{-4}), and resulting $FVF = 0.924$, i.e., in good agreement with the low level of porosity found from HRTEM and neutron radiography analysis.

The differences in the DFM results between the dynamic release (A) and quasi-static steady-state conditions (B) are hard to explain at this stage. Pressure decrease seems to stimulate the release of methane from (L). One has to consider that detachment of methane from the soot surface can be coupled to changes in the soot matrix configuration, which has some mechanical flexibility, for instance due to movements of the chains/primary particles subjected to differential force fields due to pressure gradients. Movements in the fractal structure can be expected by interactions between methane molecules and the soot material. Currently, we cannot yet test this hypothesis or give alternative explanations besides that the apparent soot density may increase (while primary particle density maintained) due to contraction of the soot material

in the region of observation during methane pressure release. Most probably, the movements are correlated on different scales and coming investigations should consider all the scales from the micro-subnanometer to macro-millimeter. Further investigations will be required to solve this puzzle, such as compacting the soot samples in order to limit soot volume expansion or contraction during pressure changes. Information on particles and pores can be achieved from X-ray and neutron scattering, SAXS and SANS (see e.g. [6] for X-ray and particles, and [30] for SANS and pores), which present different sensitivities with respect to the atomic number of species and can yield complementary information on the size distribution function and of particles and pores. X-ray and neutron scattering have also been used to determine atomic pair distribution functions and the spatial distribution of atomic species for metallic alloys employed for hydrogen storage studies [31,32]. The details of the atomic positions were obtained from the respective atomic pair distribution functions. In our case special cells would be required for these studies and deuterated methane would be essential for SANS in order to distinguish between, e.g., “accessible” and “closed” pores (see e.g. [13]). Optical infrared and Raman techniques may also be applied narrow quartz to monitor how methane changes in vibrational frequencies as they get adsorbed on the particles’ surfaces on e.g. –OH groups (see, e.g., [19,20] for FT-IR as a possible concept for diagnostics application). Inverse gas chromatography (IGC) is also a technique that should be considered for coming applications to study the adsorption properties of combustion derived porous materials. It has been applied with success on coal [33] and carbon blacks [34], and graphitized carbon black [35]. A review on IGC applications can be found in [36]. Some of these techniques may, however, be more or less limited in their application to dynamic pressure conditions, depending on the time resolution that they can provide.

In the model described by Fig.5 and in the text we used the hard sphere diameter of the free methane molecule, 4.1 Å, which is a relatively small number but comparable to the scales of the carbon structure obtained from fringe analysis based HRTEM, on soot particles. Graphitic structures with plane separation around 3.6 Å that are slightly smaller in value have been reported from both X-ray scattering

and HRTEM on soot. Larger spaces can also be found for regions with more strand-like structures on the surface of less dense soot particles, which contain folded carbon or graphene structures with diameters that may exceed 10 Å [11]. Consequently, these may act as pockets or pores on the surface, which have a higher tendency to absorb methane at higher pressures. However, from the results displayed Fig.4 d we were not able to evidence any non-linear coupling to the surrounding gas that would be described by the high-order terms, $O(p^2)$, given in Fig.5, so most probably the number of pockets were not sufficient to give any signal contribution.

In future studies it would be of interest to include measurements on porous materials with different physical and chemical properties, and to explore the dependence of temperature. The present method shows great promise for studying the mechanisms of adsorption on the surface and absorption in pores of many types of combustion derived carbon materials as well as hybrid carbon containing materials such as hybrid carbon-metal or metallo-organic frameworks [37]. In order to obtain measurable pore absorption, the first attempt in coming experiments using non-treated soot should be to significantly increase the level of compression to reduce meso- and macro interstitial space of the material and also to include lower temperatures in the investigations to encourage surface condensation.

4 Conclusion

The soot material investigated showed rather homogenous distribution between volume and surface in terms of relative carbon and oxygen composition. Independent neutron attenuation and electron/X-ray measurements on samples show that native hydrogen is readily present to levels about 14% in terms of mole fraction. “Long-range” polar-dipole like interactions between the hydrogen atoms in the methane molecules and polar groups such as carboxylic, carbonyl, hydroxyl groups etc., on the surface of the soot carbon primary particles can explain the pressure behavior under steady state conditions. In more detail, from the neutron radiography measurements and analysis we find that surface adsorption of methane on

polar groups of the soot is the most reasonable interpretation of low pressure behavior under steady state conditions. The high-pressure dependence combined with electron microscopy results suggests that the level of absorption in pores is relatively low. Analysis of the neutron radiography data utilizing the model described in this work in combination with HRTEM analysis yields a density of the primary particles, or skeletal density, which agrees reasonably with estimates obtained from helium pycnometry in the region 1.3-1.4 g cm⁻³, which results to be much lower than that typically reported for soot.

Of interest for operative conditions such as static/steady state (e.g., representing fuel storage) and methane pressure release (representing fuel delivery), we found that the methane content or *DFM* behaved differently with pressure for the two conditions: During continuous pressure release from 50 to 10 bar the methane content was observed to be less than for steady state at corresponding pressure values. We have given different suggestions for these differences, but further studies will be required to give definite answers. In any case we find that neutron radiography gives great opportunities for new studies on the interaction of pressurized hydrogenous gases with porous carbons under both steady state and dynamic conditions, which should open up for real world applications on studies related to energy storage of hydrogenous gases in pressurized tanks.

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TABLES**Table 1****List of Symbols and abbreviations**

Symbols&Abbr.	Definitions
L	Flight tube length
d	Flight tube diameter
CCD	Charge couple device
(L)	Region of interest of the sample container
(R)	Region of interest of the reference container
OA	Object area
HRTEM	High resolution transmission electron microscopy
XPS	X-ray photon spectroscopy
FT-IR-TM	Fourier transform infrared transmission microscopy
EDX	Energy dispersive X-ray spectroscopy
m	Sample mass
n	Total number of moles of atoms in the sample
x_H, x_C, x_O	Mole fractions of H, C, and O in the sample
M_H, M_C, M_O	Mole masses of H, C, and O in the sample
r_H, r_C, r_O	Mole fractions of H, C, and O in the sample from XPS and/or EDX
a_1, a_2, a_3, a_4, c	Variables used for the derivation of the mole fraction of H and the total amount of atoms in the soot sample combining XPS, EDX, and neutron attenuation measurements
V_c	Container volume of (L) and (R)
A	Neutron absorbance of the sample
A_{fresh}	Neutron absorbance of a fresh sample
m_{fresh}	Mass of a fresh sample
I	Transmitted neutron flux corresponding to the number of neutrons per area and time units
I_0	Flux of incident beam on the cell
a_{cell}	Attenuation due to the cell material
σ	Total cross section
μ	Linear attenuation coefficient
D	Sample thickness
N	Number concentration per unit volume
β	Attenuation coefficient per unit pressure and length for a gas
p	Gas pressure
$a_{cell,L}$	Attenuation due to the cell material for (L)
$a_{cell,R}$	Attenuation due to the cell material for (R)

A_L	Absorbance due to gas species in (L)
A_R	Absorbance due to gas species in (R)
I_L	Transmitted neutron flux corresponding to the number of neutrons per area and time units for (L)
I_R	Transmitted neutron flux corresponding to the number of neutrons per area and time units for (R)
γ_L	$I_{L,He} / I_{L,Me}$
β_L	Attenuation coefficient per unit pressure and length for a gas in (L)
β_R	Attenuation coefficient per unit pressure and length for a gas in (R)
R	Gas constant
T	Absolute temperature
N_A	Avogadro's number
A_{Soot}	Absorbance of the soot sample
DFM	A_L / A_R , Degree of filling of methane in (L)
SVF	Soot volume fraction
FVF	1- SVF , Free volume fraction
ρ_p	Primary particle density
A_s	Soot surface
η	Probability of the soot surface being covered by methane molecules
N_p	Number of primary particles
N_{mso}	Total number of methane molecules that can cover the soot surface
N_{ms}	Resulting number of methane molecules adsorbed/absorbed by the soot
N_{mf}	Number of methane molecules in the (Interstitial) free space of the soot matrix
OC	Organic carbon
IGC	Inverse gas chromatography

Table 2

Summary of soot properties related to structure and adsorption/absorption

Class	Properties
(I)	<p><u>Potentially related to absorption</u>: Micro-pore ($D < 2$ nm). More specifically, ultra-micro pores ($D < 0.7$ nm) and super-micro pores ($0.7 \text{ nm} < D < 2 \text{ nm}$):</p> <p>(i). Nano-pores (“radial”) and nano-pockets (“tangential”) at the surface, <u>accessible</u> to the gas phase that can take part in the absorption process. Their number seem to be limited in the investigated sample and may be hard to evidence in this study.</p> <p>(ii). Voids, <u>closed and isolated</u>, in the internal regions of primary particles not active in the absorption processes.</p>
(II)	<p>Meso ($2 \text{ nm} < D < 50 \text{ nm}$)- and macro-pores ($D > 50 \text{ nm}$) scales: For soot material the meso- and macro-scales are mainly part of the interstitial free space of the material matrix and more related to “open” structures than pores. Due to the mechanical flexibility of the material the sizes of these and the average distances between the primary particles can be decreased and thus the total material surface density be increased by compressing the material. From the HRTEM images on uncompressed samples we observed 2-D projections with sizes from ca 10 nm and larger.</p>
(III)	<p><u>Related to adsorption</u>: Surface polar, oxygen containing groups, in particular distributed -OH, that can have important attractive properties for methane. Our XPS and FT-IR-TM measurements show the presence of not only such groups, but also other oxygenated groups with polar properties. Surface polar groups may be the most active mediators for attraction and uptake of methane by the soot material.</p>

Table 3

Cross sections for attenuation at 2.6 Å (1barn = 10^{-24} cm²).

Atomic species ^a	σ_{scat}^b	σ_{abs}^c	σ_{abs}^d	σ_{att}^e
H	82.02	0.3326	0.4809	82.50
He	1.34	0.00747	0.0108	1.351
C	5.551	0.0035	0.0051	5.556
O	4.232	0.00019	0.0002747	4.232
CH ₄	333.631	1.3339	1.9287	335.6 ^f

^aNatural isotope composition.

^bElastic scattering cross section data from source [22].

^cAbsorption cross section data for thermal neutrons from the source [22].

^dAbsorption cross section recalculated for 2.6Å, $\sigma_{abs}^d = \sigma_{abs}^c \cdot 2200/1522$; thermal velocity = 2200 m/s; cold velocity = 1522 m/s

^eAttenuation cross section for 2.6Å, $\sigma_{att}^e = \sigma_{scat}^b + \sigma_{abs}^d$.

^f $\sigma_{att}(\text{CH}_4) = \sigma_{att}(\text{C}) + 4 \times \sigma_{att}(\text{H})$.

Table 4

a - and b -coefficients of η used for conditions A-H and the corresponding values of ρ_p .

Conditions labels ^a	a^b	b^c	a/b^d	ρ_p^e	FVF	$Composition^f$ (H,C,O)
A	2.50×10^{-4}	7.47×10^{-3}	0.033	2.00	0.843	0.00, 1.00, 0.00
B	2.00×10^{-3}	7.47×10^{-3}	0.268	2.00	0.843	0.00, 1.00, 0.00
C	5.00×10^{-3}	7.47×10^{-3}	0.669	2.00	0.843	0.00, 1.00, 0.00
D	2.50×10^{-4}	0.00	-	2.00	0.843	0.00, 1.00, 0.00
E	2.00×10^{-3}	0.00	-	2.00	0.843	0.00, 1.00, 0.00
F	5.00×10^{-3}	0.00	-	2.00	0.843	0.00, 1.00, 0.00
G	2.50×10^{-4}	0.00	-	1.37	0.926	0.14, 0.80, 0.06
H	2.50×10^{-4}	4.23×10^{-3}	0.059	0.96	0.894	0.14, 0.80, 0.06

^aLabels given in Fig.6 and the related text.

^bThe coefficient a in Eq. (18).

^cThe coefficient b in Eq. (18) in bar^{-1} .

^dRatio of the coefficients a and b .

^ePrimary particle mass density in g cm^{-3}

^fAssumed composition of atomic species H, C, and O of primary particles.

FIGURES

Fig.1

Fig. 1. a) Front view photograph of the Swagelok cross placed in front of the detector showing the placement of the aluminum containers (L) and (R) in the cross; b) background compensated and beam flux normalized transmission radiograph for 4.9 bar helium, and c) 51.5 bar methane; d) is ratio between images b) and c). The images b) and c) were rotated by 2.5° counterclockwise.

Fig.2

Fig.2. Electron microscopy image of the soot particles.

Fig.3

Fig. 3. Series of FTIRTM spectra obtained for grains of soot material similar to the one used in the experiment. Region 1) is the fingerprint region where C-H bending and skeletal bound oxygen may appear; 2) aromatic C-C stretch, 3) carbonyl (C=O) stretch; 4) aliphatic C-H stretch; 5) O-H stretch. Each curve corresponds to an individually sampled transmission area of $30\ \mu\text{m} \times 30\ \mu\text{m}$. The measurements were performed at beamline D7, MAX-lab, Lund.

Fig.4

Fig. 4. Results from a) Dynamic release measurements of methane (A); b) $A_{Me,R} - A_{Me,L}$ vs. pressure for condition (A) and quasi static condition (B); c) $A_{Me,R}$ for (B); and d) DFM vs. pressure for (A) and (B) together with linear fits based on linear regression and the theoretical description given in the text. The value for helium assuming soot of only carbon and $\rho_p = 2 \text{ cm}^{-3}$ is also given.

Fig.5

Fig. 5. Evaluating the interaction between methane and the soot particles.

Fig.6

Fig. 6. Calculated values of DFM vs pressure for different a - and b -coefficients given in Table 4: a) Cases A-C with $b = 7.47 \times 10^{-3}$; b) Cases D-F with $b = 0.00 \times 10^{-3}$. Cases G and H yield curves very similar to case A and are therefore not reported in this figure. The data sets DFM_SS and DFM_GR stand for the DFM under steady state and gradual release conditions, respectively.