Quarterly Report

Fundamental Understanding of Methane-Carbon Dioxide-Water (CH_4-CO_2-H_2O) Interactions in Shale Nanopores under Reservoir Conditions

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WORK PERFORMED UNDER

Field Work Proposal 14-017608

PRINCIPAL INVESTIGATOR

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1.0 GOALS OF PROJECT

Shale is characterized by the predominant presence of nanometer-scale (1-100 nm) pores. The behavior of fluids in those pores directly controls shale gas storage and release in shale matrix and ultimately the wellbore production in unconventional reservoirs. Recently, it has been recognized that a fluid confined in nanopores can behave dramatically differently from the corresponding bulk phase due to nanopore confinement (Wang, 2014). CO_2 and H_2O, either preexisting or introduced, are two major components that coexist with shale gas (predominately CH_4) during hydrofracturing and gas extraction. Note that liquid or supercritical CO_2 has been suggested as an alternative fluid for subsurface fracturing such that CO_2 enhanced gas recovery can also serve as a CO_2 sequestration process. Limited data indicate that CO_2 may preferentially adsorb in nanopores (particularly those in kerogen) and therefore displace CH_4 in shale. Similarly, the presence of water moisture seems able to displace or trap CH_4 in shale matrix. Therefore, fundamental understanding of CH_4-CO_2-H_2O behavior and their interactions in shale nanopores is of great importance for gas production and the related CO_2 sequestration. This project focuses on the systematic study of CH_4-CO_2-H_2O interactions in shale nanopores under high-pressure and high temperature reservoir conditions. The proposed work will help to develop new stimulation strategies to enable efficient resource recovery from fewer and less environmentally impactful wells.

2.0 ACCOMPLISHMENTS

Experimental Work

We measured the P-V-T-X properties of CH_4-CO_2 mixtures with CH_4 up to 95 vol. %, and adsorption kinetics of various materials, under the conditions relevant to shale gas reservoir. We use three types of materials: (I) model materials, (II) single solid phases separated from shale samples, and (III) crushed shale samples. The model materials are well characterized in terms of pore sizes. Therefore, the results associated with the model materials serve as benchmarks for our model development.

The P-V-T-X properties obtained in this study will be used to establish a high precision equation of state (EOS) applicable to shale gas recovery in confined nano-pore environments. An equation of state (EOS) that can accurately describe interactions in the CH_4–CO_2–H_2O system for a wide range of ionic strengths in a confined environment is an important and essential tool that enables efficient resource recovery from fewer and less environmentally impactful wells. However, such an EOS does not exist at present. For the bulk properties, Duan et al. (1992) proposed an EOS for the CH_4–CO_2–H_2O system. Their EOS was based almost solely on experimental data for binary systems (e.g., CH_4–H_2O, CO_2–H_2O, and CH_4–CO_2). As they pointed out, "ternary data are almost nonexistent." In their parameterization, there were two experimental investigations addressing the ternary system. Price (1981) measured solubility of CH_4 and CO_2 in brine containing 5 wt% NaCl at 150^oC and 345 bars. Ramboz et al. (1985) investigated the CH_4–CO_2–H_2O system at temperatures above 370^oC, which is not applicable to the conditions for shale gas recovery. After the publication of Duan et al. (1992), a number of studies on the CH_4–CO_2–H_2O system below room temperature were initiated. The aim of these studies was to determine the hydrate equilibrium (e.g., Bruusgaard et al., 2010), but again these studies are not relevant to the conditions applicable for shale gas recovery.

Sorption capacities, sorption and desorption kinetics are highly relevant to shale gas recovery. We systematically measured sorption capacities, sorption and desorption kinetics for the afore-mentioned three types of materials under reservoir relevant conditions. These results will be used for molecular dynamics (MD) modeling of the interactions in a multiple component system.

We employed the gravimetric method using a Netzsch STA 409 thermal gravimetric analyzer (TGA) with differential scanning calorimeter (DSC) and Differential temperature analyzer (DTA) that is adapted for measurement of adsorption capacities and kinetics of the three types of materials at reservoir relevant temperatures up to 125^{o}C and constant pressures up to 1 bar. We studied the adsorption kinetics by monitoring the evolution of the weight change as a function of time from the instant a dose of CO_2 and CH_4 gas mixture was adsorbed onto the sample, until the moment saturation equilibrium was reached.

Table 1. Experimental measurements of sorption capacities and sorption rates for the model substances at 1 bar total pressure

Model Substances	Temp, ^{o}C	Gas Mixture, volume percent	Pressure, bar	Sorption Capacity, mg/g	Sorption Rate, mg/g min^{-1}
DARCO activated carbon	25	85% CH_4 + 15% CO_2	1	28	0.68
	50	85% CH_4 + 15% CO_2	1	11	0.59
	75	85% CH_4 + 15% CO_2	1	9.0	0.31
	100	85% CH_4 + 15% CO_2	1	2.1	0.14
	125	85% CH_4 + 15% CO_2	1	1.8	0.10
Montmorillonite, <75 μm	25	85% CH_4 + 15% CO_2	1	2.8	4.7×10^{-2}
	50	85% CH_4 + 15% CO_2	1	0.30	9.6×10^{-3}
	75	85% CH_4 + 15% CO_2	1	0.19	6.7×10^{-3}
	100	85% CH_4 + 15% CO_2	1	0.18	5.1×10^{-3}
	125	85% CH_4 + 15% CO_2	1	0.12	3.3×10^{-3}
Crushed Shale	25	85% CH_4 + 15% CO_2	1	0.29	3.3×10^{-3}
	50	85% CH_4 + 15% CO_2	1	0.21	2.7×10^{-3}
	75	85% CH_4 + 15% CO_2	1	0.16	1.7×10^{-3}

We here also report the preliminary results regarding sorption capacities and kinetics for the model substances at high temperatures and pressures using the instrumentation designed at SNL. The system developed at SNL uses digital transducers for data acquisition. The digital transducers are calibrated with the high precision Heise gauge (see Figures 1 and 2).

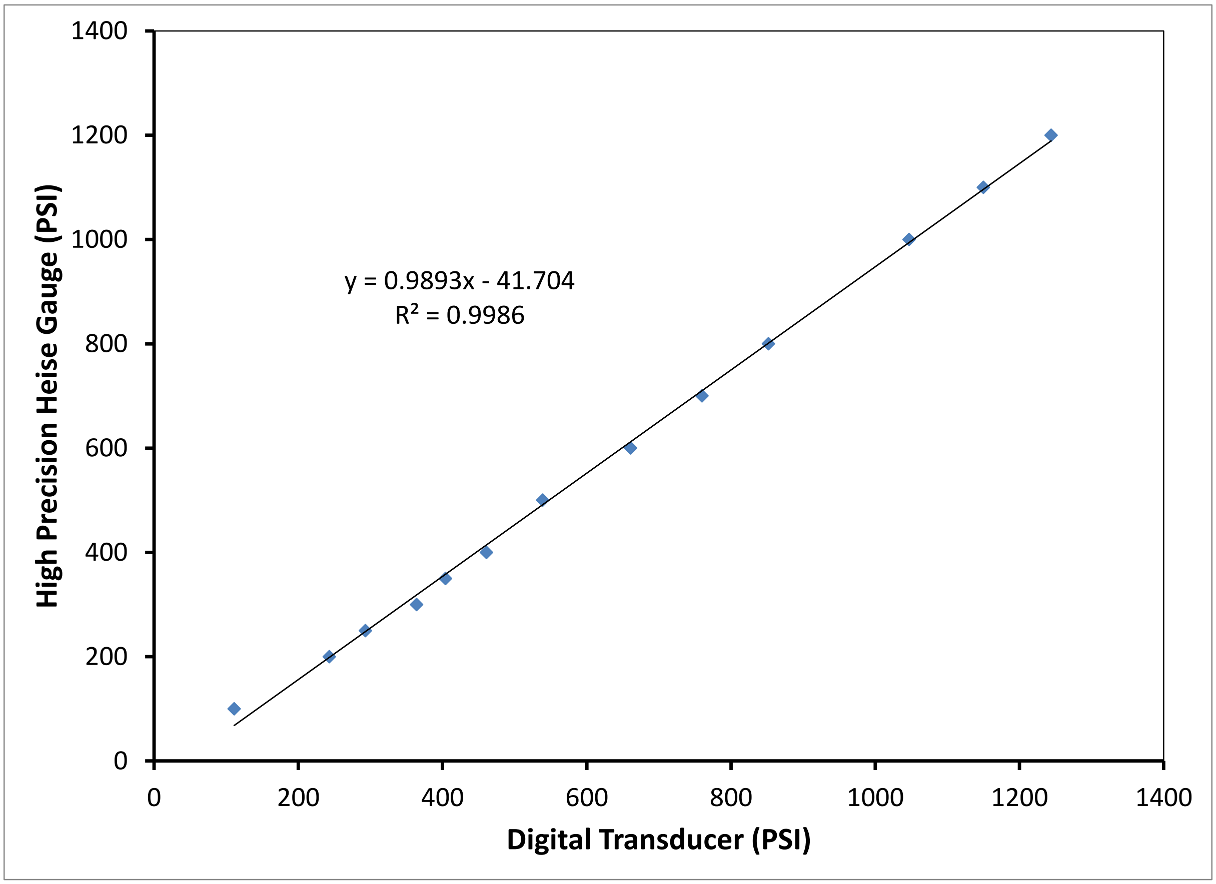

Figure 1. Calibration of the digital transducer for the reference cell of the system for measurement of sorption capacities and kinetics

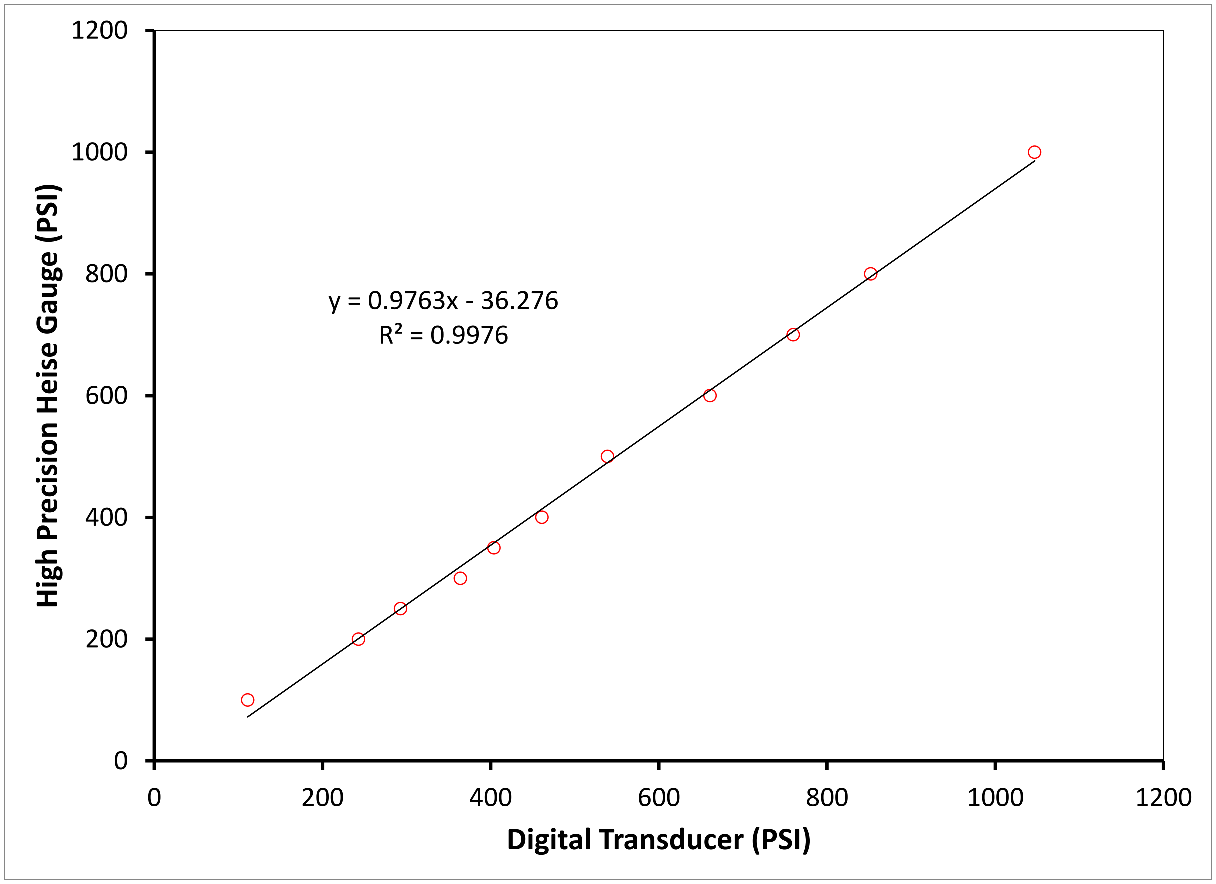

Figure 2. Calibration of the digital transducer for the sample cell of the system for measurement of sorption capacities and kinetics

In Figure 3, a typical sorption curve using TGA is presented. The linear portion of the curve is used for determination of sorption kinetics. The portion that indicates the sorption saturation has been attained is used for determination of sorption capacities. As an example, the sorption rate for montmorillonite is determined from the linear portion of the sorption curve as shown in Figure 4. We have used this methodology to measure the sorption capacities and kinetics for activated carbon, crushed shale, mesoporous silica, illite and montmorillonite. We have obtained raw data for these materials up to 125^{o}C. The sorption capacities and sorption rates that have been processed so far are listed in Table 1.

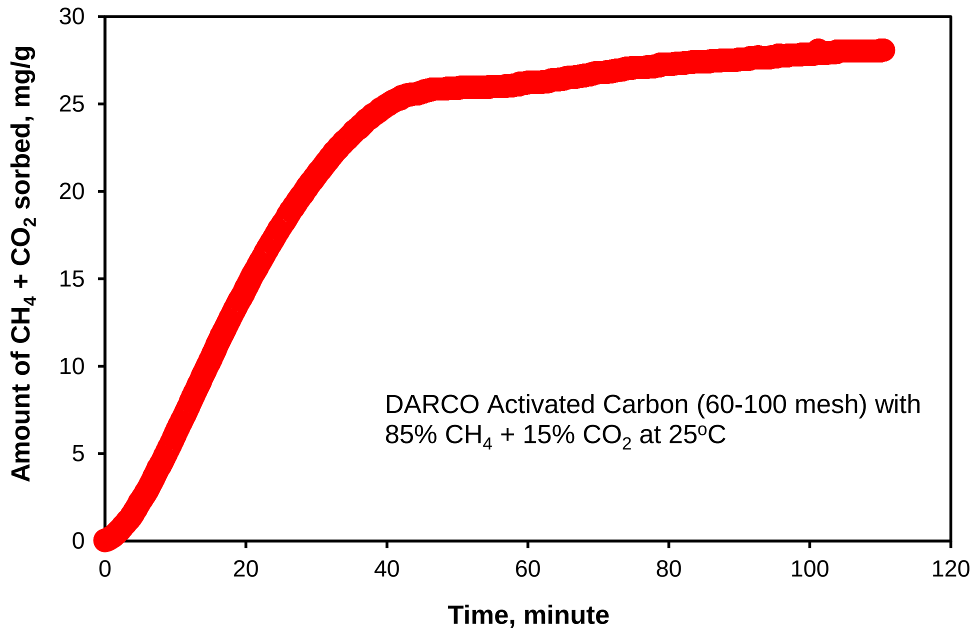

Figure 3. Sorption of CH_4 + CO_2 onto activated carbon at 25^{o}C temperature and 1 bar

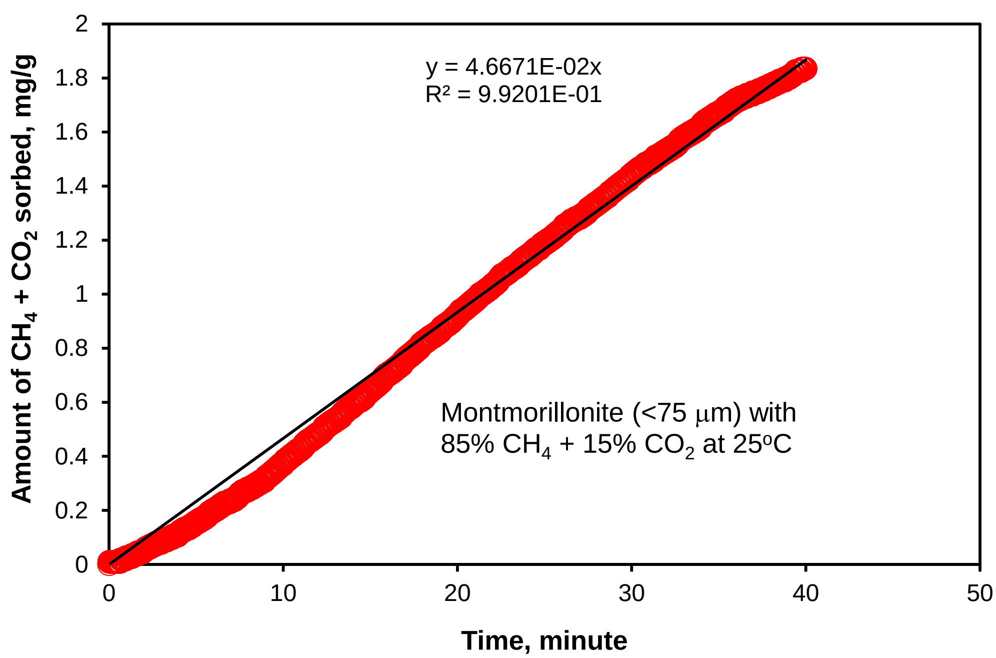

Figure 4. Sorption kinetics with CH_4 + CO_2 for montmorillonite at 25^{o}C temperature and 1 bar

In Figure 5, a typical sorption curve at high temperatures and pressures using the instrumentation designed at SNL is presented. The decrease in pressure is interpreted as absorption to adsorbent materials. The amounts of absorbed are calculated based in the differential pressure according to the compressibility factor of CH_4+CO_2 mixtures at the experimental temperature:

$$Z = \frac{P \times V}{n_{Total} \times R \times T}$$

McElroy et al. (1989) measured the compressibility factors for CH_4+CO_2 mixtures at CH_4 percentages of 0, 25, 75 and 100 in the temperature range from 30^{o}C to 60^{o}C. We used their measured compressibility factor at 50^{o}C to calculate the amounts absorbed and the sorption kinetics (Table 2).

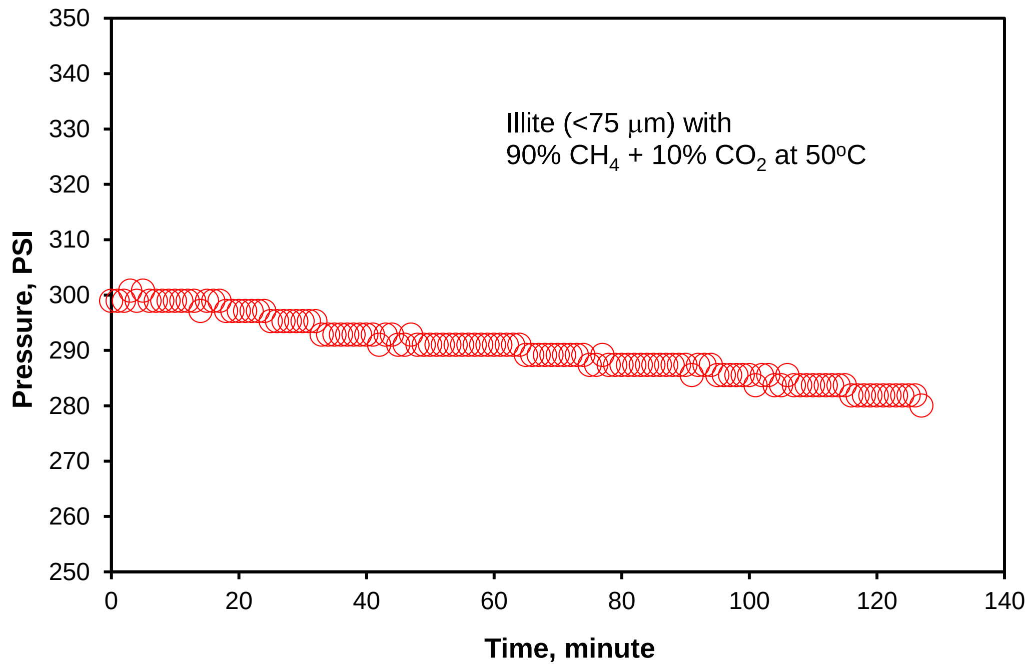

Figure 5. Sorption of CH_4 + CO_2 onto illite at 50^{o}C temperature and 300 psi

Table 2. Experimental measurements of sorption capacities and sorption rates for the model substances at elevated temperatures at pressures

Model Substances	Temp, ^{o}C	Gas Mixture, volume percent	Pressure, PSI	Sorption Capacity (mixture) mg/g	Sorption Rate, mg/g min^{-1}
Illite, <75 μm	50	90% CH_4 + 10% CO_2	300	160	6×10^{-1}

We have obtained raw data for the model materials up to 125^{o}C and at the total pressures of 1000 psi by using the same method. We are looking for the literature compressibility data for our system, and process our measured compressibility factors. The results will be provided in the next quarterly report.

Modeling Work

Models for amorphous silica, montmorillonite and kerogen have been selected and created for simulation with individual and mixed gases. For kerogen, a representative suite of models that span a range of maturity have been developed by Ungerer et al. (2014). These models are now being studied with different force fields (e.g., OPLS, PCFF, CVFF) to determine which one will best predict the physical properties of both kerogen and methane as a function of temperature and pressure. Figure 6 illustrates an initial configuration containing kerogen molecules representative of the mature end member of the organic-rich Duvernay series. This conformation is being relaxed in successive NPT stages (900K, 700K, 500K, and 400K) in order to compare our software's results to that used by Ungerer et al. (2014). This will also result in one of the initial kerogen configurations to examine gas adsorption and diffusion. In August, a postdoctoral associate will join our team and conduct matrices of simulations using the force fields and models currently being tested.

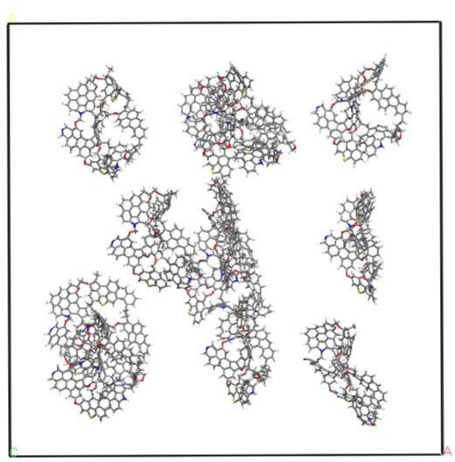

Figure 6. Initial configuration containing kerogen molecules representative of the mature end member of the organic-rich Duvernay series

As a part of an effort to understand how surface functional groups affect CH_4-CO_2-H_2O sorption on carbonaceous materials (such as kerogen), density functional theory calculations have been carried out using the VASP code within the generalized gradient approximation with the Perdew-Burke-Ernzerhof exchange-correlation functional (GGA/PBE) for the structural optimization and adsorption of COOH, OH and SH functional groups at the edge of a hydrogen-terminated (7,0) SWCNT (cf. Figure 1). The computed bond distances between the functional groups and the non-hydrogen terminated, dangling carbon atom at the edge of the (7,0) SWCNT are: d(C–COOH) = 1.49 Å, d(C–SH) = 1.76 Å, d(C–OH) = 1.36 Å, d(C–NH3) = 1.48 Å. The functional groups are covalently binding the edge of the SWNCT, as shown by the continuous electron density (yellow) depicted in Figure 1. The binding energies of the various functional groups were calculated by fully relaxing simultaneously both the SWCNT and the functional group as follows: E_b = E(CNT+group) – E(CNT) – E(group), where E(CNT+group), E(CNT) and E(group) are the total energies of the CNT and functional group system, the isolated CNT and the isolated functional group, respectively. The binding energies are: 3.88 eV for COOH, 4.07 eV for OH and 3.01 for SH.

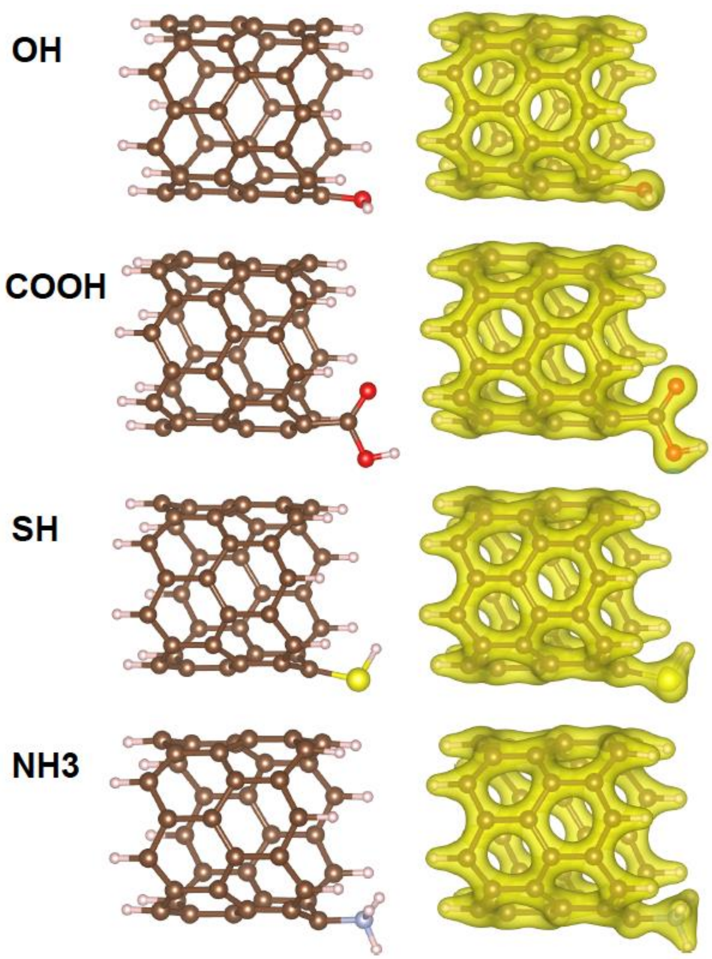

Figure 7. Optimized structures showing the formation of covalent bonds between the OH, COOH, SH and NH_3 functional groups and the edge of a (7,0) zigzag SWCNT with hydrogen

termination. The electron density is represented by the yellow isosurface.

3.0 OUTLOOK

The next step will include:

- Expanding the low pressure sorption measurements to a full cycle of adsorption-desorption measurements. The data to be obtained will help understand the possible hysteresis behavior of gas sorption in nanopores.
- Continue performing high pressure and high temperature sorption measurements. Develop a highly accurate equation of state (EOS) for CH_4-CO_2 mixtures for data interpretation.
- Starting a cDFT formulation for CH_4-CO_2 sorption in nanopores and trying to apply the model to both low and high pressure measurements.

4.0 REFERENCES

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