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Sefan Iglauer
Edith Cowan University

Hussein Abid
Edith Cowan University

Ahmed Z. Al-Yaseri
Edith Cowan University

Alireza Keshavarz
Edith Cowan University

Correspondence to:
S. Iglauer and H. Abid,
s.iglauer@ecu.edu.au;
h.alfatlawi@ecu.edu.au

Hydrogen Adsorption on Sub-Bituminous Coal: Implications for Hydrogen Geo-Storage

Stefan Iglauer[1] (ID)**, Hussein Abid[1]** (ID)**, Ahmed Al-Yaseri[1], and Alireza Keshavarz[1]**

[1]Petroleum Engineering Discipline, School of Engineering, Edith Cowan University, Perth, WA, Australia

Abstract Hydrogen is a clean fuel that can potentially revolutionize the energy supply chain and decarbonize fuel consumption. However, a key hurdle that needs to be overcome before a full-scale hydrogen economy can be established is hydrogen storage which is currently the main limitation. Here, we propose that hydrogen gas can be stored in underground coal seams, where it adsorbs on the coal surface. However, currently, no hard data related to such a procedure exists. We, therefore, demonstrate experimentally that significant amounts of hydrogen gas can be stored via this route. Hydrogen adsorption capacities reached 0.6 moles H_2/kg of coal at 14.3 MPa, and adsorption capacity initially increased strongly with pressure (up to ~4 MPa) and then plateaued out, while temperature only had a very minor influence. This study provides fundamental data for hydrogen storage in coal seams, and thus aids in the industrial implementation of a hydrogen supply chain.

Plain Language Summary Hydrogen is a clean fuel which can potentially revolutionize the energy supply chain and decarbonise fuel consumption. However, a key hurdle which needs to be overcome before a full-scale hydrogen economy can be established is hydrogen storage which is currently the main limitation. Here, we propose that hydrogen gas can be stored in underground coal seams, where it adsorbs on the coal surface. We demonstrate experimentally that significant amounts of hydrogen gas can be stored via this route. This work provides fundamental data for hydrogen storage in coal seams, and thus aids in the industrial implementation of a hydrogen supply chain.

1. Introduction

Hydrogen is a clean fuel that can potentially revolutionize the energy supply chain and decarbonize fuel consumption (Hanley et al., 2018; Tarkowski, 2019). However, hydrogen storage is currently the key hurdle that prevents the establishment of an industrial-scale hydrogen economy (Berta et al., 2018; Flesch et al., 2018; Heinemann et al., 2018; Iglauer et al., 2021; Lord et al., 2014; Shi et al., 2020; Tarkowski & Czapowski, 2018; Yekta et al., 2018; Zhang et al., 2016). It is, thus, necessary to develop better hydrogen-storage solutions (Zhang et al., 2016). One new concept is the storage of hydrogen gas in underground coal seams, where hydrogen adsorbs on the coal surface and can be withdrawn again at any time when required. This concept is analog to methane storage in such geologic underground coal seams. Methane is adsorbed on the coal surface over geologic times, and it is now a resource produced via coal bed methane (CBM) production (e.g., Moore, 2012; Seidle, 2011). Connected with that is also enhanced CBM production, where CO_2 is injected into a deep coal seam; the CO_2 displaces more methane while it is itself adsorbed on the coal surface (Chaturvedi & Sharma, 2020; Keshavarz et al., 2017).

However, while CH_4 and CO_2 adsorption has been extensively studied to optimize CBM, no data are available for hydrogen adsorption on coal. We, therefore, measured H_2 adsorption on a typical sub-bituminous coal sample, and demonstrate that substantial amounts of H_2 can be stored via this approach, even at moderate pressures. This study will thus aid in the larger-scale implementation of a hydrogen economy.

2. Experimental Procedure

Sub-bituminous coal (Pan Upper, supplied by Premier Coal located in Collie, Western Australia; maximum vitrinite reflectance: 0.38%) was selected and thoroughly analyzed for its essential properties (Table 1). In addition, the coal was characterized via Thermal Gravimetric Analysis (TGA) and the coal surface was characterized via Fourier-Transformed Infrared Spectroscopy (FTIR) and energy dispersive spectroscopy, the

Table 1
Essential Analysis Properties of Pan Upper Raw Coal

| Proximate analysis (wt %)			
Inherent moisture	Ash	Volatile matter	Fixed carbon
21.7	2.5	28.0	47.8
Ultimate analysis (wt%)			
Carbon	Hydrogen	Nitrogen	Relative density (%)
58.1	2.98	1.15	1.39
Maceral composition (volumetric, %)			
Vitrinite	Liptinite (Exinite)	Inertinite	Mineral matter
33.3	11.3	43.9	11.5

detailed results can be found in the Supporting Information. The coal was then crushed with a blade grinder and sieved to a homogeneous particle size (<250 μm). Low-pressure N_2 (99.999 vol%) BET adsorption and desorption curves and the zeta potential of the coal powder were then measured to further characterize the coal surface. Note that the zeta potential was measured with a Zetasizer Nano ZS in deionized water at pH = 8.7, 0.1 MPa, and 296 K. For more details regarding the TGA, FTIR, and N_2 BET measurements, please see the Supporting Information.

Subsequently, the adsorption profiles of CO_2 (purity = 99.99 mol%) and H_2 (purity = 99.995 mol%) were measured at elevated temperatures and a wide pressure range (0.1–14.3 MPa) using a PCTpro adsorption analyzer (Setaram Instrumentation). The average standard deviation of the high-pressure adsorption experiments was estimated as ±7.3% (H_2) and 8.0% (CO_2), based on replicate measurements.

3. Results and Discussion

Clearly, H_2 adsorption increased dramatically with increasing pressure, Figure 1. Initially, this increase was very steep, but the adsorption curve plateaued out at ~4 MPa. Thus, at low pressure (0.1 MPa), only small amounts of H_2 could be adsorbed (0.005 moles/kg coal), while at 3.38 MPa, 0.23709 moles H_2/kg coal were adsorbed (both measured at 303 K), a 47,418-fold increase. The H_2 amount adsorbed increased further to 0.54686 moles H_2/kg coal at 11.74 MPa (at 303 K) and 0.60183 moles H_2/kg coal at 14.3207 MPa (at 318 K), a 120,000-fold increase. Such a type I adsorption curve indicates the presence of micropores (which is expected in coal; Okolo et al., 2015) and that H_2 was adsorbed as a mono-layer (Singh et al., 1985). This is in contrast to the low-pressure N_2-BET adsorption profiles which indicated a type II adsorption system (compare the Supporting Information), thus N_2 was adsorbed in multiple molecular layers on the coal surface at low pressure. Note that the type II N_2-isotherm was caused by N_2 condensing in narrow pore throats, as N_2 boiling temperature (at atmospheric pressure) is 77 K (and the experiment was performed at 77 K) (Flores, 2014). Furthermore, changes in temperature (from 303 to 333 K) only slightly influenced the adsorption profile (a marginally smaller amount of H_2 was adsorbed at the higher temperature). We conclude that substantial amounts of H_2 can be stored in deep coal seams where high pressures and elevated temperatures prevail.

However, approximately 10 times the amount of CO_2 could be adsorbed (e.g., 2.64 moles of CO_2/kg coal at 3.302 MPa vs. 0.23709 moles of H_2/kg coal at 3.382 MPa, both measured at 303 K). This is mainly related to the very low zeta potential of the coal (−70 mV measured at pH 8.7, 296 K, and 0.1 MPa in deionized water). Such a high negative surface charge will strongly interact with a molecule that has a high quadrupole moment (the CO_2 quadrupole moment is -4.3×10^{-26} esu.cm²; Buckingham et al., 1968). Note that CO_2 can also undergo Lewis acid-base reactions because of this high quadrupole moment, and form hydrogen bonds with alcohol or carbonyl groups (Raveendran et al., 2005; Fujii et al., 2002). As coal is a very complex organic material (Hatcher & Clifford, 1997), the coal tested also contained alcohol and carbonyl groups (compare the infrared spectra in the Supporting Information); these groups further strengthened the affinity (and thus adsorption) between CO_2 and coal. This is in contrast to H_2 which also has no external electric dipole moment and a quadrupole moment which is one magnitude smaller ($+0.651 \times 10^{-26}$ esu.cm²; Buckingham
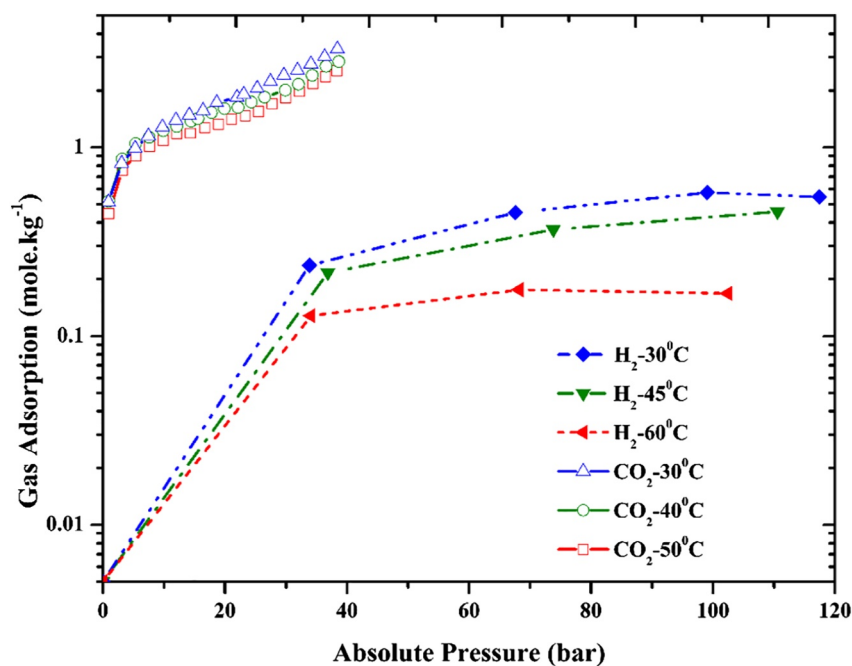
Figure 1. Hydrogen adsorption on sub-bituminous coal as a function of pressure and temperature. Data for CO_2 have been added for comparison.

et al., 1968). H_2 adsorption onto the coal surface is therefore driven by dispersive (non-polar–non-polar interactions, that is, induced dipole moment – induced dipole moment interactions) Van der Waals forces only, which in total are substantially weaker than the total interaction forces between CO_2 and the coal surface. This weaker interaction between the H_2 and the coal surface results in reduced H_2 adsorption capacity.

4. Conclusions

Hydrogen storage is currently a key barrier to the implementation of an industrial-scale hydrogen economy. We, therefore, examined here the potential of hydrogen storage in underground coal seams, where H_2 could be stored as an adsorbed phase on the coal surface. Indeed, this is possible from a fundamental technical perspective as we demonstrated via laboratory adsorption experiments. Substantial amounts of H_2 (0.23709 moles H_2/kg coal) could be stored at moderate pressure and temperature (303 K and 3.3 MPa, note that these thermo-physical conditions prevail at a depth of approximately 300 m; Dake, 1978); this adsorption capacity could be further enhanced at higher pressures (14.3 MPa) to 0.60183 moles H_2/kg coal (at 318 K). We conclude that hydrogen storage in deep coal seams is potentially possible, this study, therefore, supports the large-scale set-up of a hydrogen supply chain.

Conflict of Interests

The authors declare that there are no conflict of interests.

Data Availability Statement

Adsorption data for H_2 and CO_2 as functions of pressure and temperature are available at https://ro.ecu.edu.au/datasets/56/.

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