

8-29-2022

Effects of various solvents on adsorption of organics for porous and nonporous quartz CO₂ brine systems: Implications for CO₂ geo-storage

Muhammad Ali
Edith Cowan University, m.ali@ecu.edu.au

Nurudeen Yekeen

Mujahid Ali
Edith Cowan University, mujahid.ali@ecu.edu.au

Mirhasan Hosseini
Edith Cowan University, m.hosseini@ecu.edu.au

Nilanjan Pal

See next page for additional authors

Follow this and additional works at: <https://ro.ecu.edu.au/ecuworks2022-2026>

 Part of the [Chemical Engineering Commons](#)

[10.1021/acs.energyfuels.2c01696](https://doi.org/10.1021/acs.energyfuels.2c01696)

Ali, M., Yekeen, N., Ali, M., Hosseini, M., Pal, N., Keshavarz, A., ... & Hoteit, H. (2022). *Effects of Various Solvents on Adsorption of Organics for Porous and Nonporous Quartz/CO₂: Implications for CO₂ Geo-Storage*. *Energy & Fuels*, 36(18), 11089-11099.

<https://doi.org/10.1021/acs.energyfuels.2c01696>

This Journal Article is posted at Research Online.

<https://ro.ecu.edu.au/ecuworks2022-2026/1262>

Authors

Muhammad Ali, Nurudeen Yekeen, Mujahid Ali, Mirhasan Hosseini, Nilanjan Pal, Alireza Keshavarz, Stefan Iglauer, and Hussein Hoteit

Effects of Various Solvents on Adsorption of Organics for Porous and Nonporous Quartz/CO₂/Brine Systems: Implications for CO₂ Geo-Storage

Muhammad Ali,* Nurudeen Yekeen, Mujahid Ali, Mirhasan Hosseini, Nilanjan Pal, Alireza Keshavarz, Stefan Iglauer, and Hussein Hoteit*



Cite This: *Energy Fuels* 2022, 36, 11089–11099

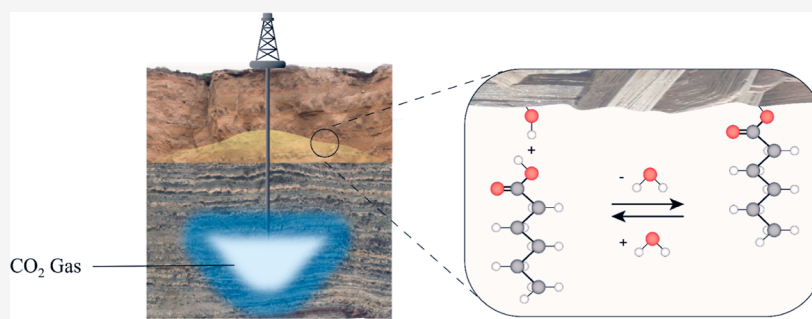


Read Online

ACCESS |

Metrics & More

Article Recommendations



ABSTRACT: The underground geo-storage of carbon dioxide (CO₂) is an essential component of the carbon capture and sequestration value chain. The success of CO₂ containment depends on the wetting state of the rock, which controls the mechanism of fluid flow and distribution. The presence of organic acids in the storage formation introduces a considerable effect on the wettability of the rock/CO₂/brine system under various temperature and pressure conditions. Despite the previous studies on this topic, the impact of the substrate pores, the rock surface roughness, and the solvents used to prepare the organic acid solution under various temperatures and pressures has not yet been elucidated. In the present study, the contact angles of non-porous quartz and porous Fontainebleau quartz are measured in CO₂/brine systems at various pressures of 0.1–20 MPa and temperatures of 298 and 323 K. In addition, various solvents are used to prepare the stearic acid solution in order to assess their influence on the adsorption of organics for porous and non-porous quartz/CO₂/brine systems. The results clearly indicate that *n*-decane is the most effective solvent for solubilizing the stearic acid to attain full wettability of the substrate by CO₂ due to its polar compatibility with the stearic acid. Generally, the porous aged Fontainebleau quartz exhibits higher contact angles than the aged non-porous quartz at higher pressures, and the unaged Fontainebleau surfaces demonstrate water wettability, with a wide range of advancing and receding contact angles of less than 90°. However, when the pressure is increased to 15 and 20 MPa in the CO₂/brine system, the contact angles of the Fontainebleau quartz are higher than those of pure quartz. These results suggest that the surface roughness of the rock merely amplifies the inherent surface chemistry and original wettability of the rock if surface conditions are hydrophobic.

1. INTRODUCTION

The greenhouse effect has contributed significantly to the rise in the Earth's temperature and global warming.^{1–4} One of the key gases responsible for the greenhouse effect is carbon dioxide, which is produced mainly from fossil-fuel combustion and oxidation.^{1,5} Almost 36 billion tons of anthropogenic CO₂ emissions per annum have been attributed to stationary and non-stationary fossil fuel sources.^{1,6} While alternative solutions have been proposed,^{7–14} CO₂ capture and storage are regarded as a means for attaining the de-carbonization objectives and restraining the global rise in temperature to less than 2 °C.^{15–19} Nevertheless, the storage process is very complex and requires a fundamental understanding of the fluid flow

dynamics, rock-fluid interfacial interactions, storage/caprock wetting states, trapping capacities, and containment security of various geological storage formations.^{20–27}

The CO₂ wettability of reservoir rock and rock-fluid interfacial tensions are important properties that affect the pore-space fluid flow and fluid distribution during geological

Received: May 24, 2022

Revised: August 9, 2022

Published: August 26, 2022



CO₂ storage.^{28–31} Previous studies have demonstrated that as the affinity of the storage rock toward the CO₂ phase increases, its capillary/residual trapping capacity decreases. At the same time, the risk of gas leakage through the caprock increases, thereby decreasing its structural trapping potential.^{32–37} Meanwhile, increasing concentrations of the organic contaminants that are inherent in reservoir rocks have been shown to decrease the water-wettability thereof^{38–41} due to increasingly hydrophobic conditions. The geo-storage formations contain organic acids due to hydrocarbon biodegradation,^{42,43} diagenesis of organic matter, and relocation into water-dominated zones.³⁸ These organic molecules have been discovered in various geological formations, and their carbon components can range from C₂ to C₂₆.^{43–46} The existence of organic acids in geological formations is theorized to result from the evolution of hydrocarbons from organic and/or biological substances possessing similar structures at the molecular level.^{44,46} A change in the wettability from hydrophilic (water-wet) to hydrophobic conditions arises from the esterification^{33,39,47} of organics on the –OH group of quartz-containing rocks via covalent chemical bonding (condensation reactions).^{33,38,39} Various experimental investigations on the effects of organic acid contamination upon rock wettability in a CO₂/brine environment have commonly used volatile organic compounds (VOCs) such as ethanol, methanol, and decane as the solvents for the preparation of various organic acid solutions. In most of the existing studies, the rock substrates have been aged by exposure to *n*-decane/stearic acid solution for a sufficient period for the acid to be adsorbed on the rock in order to simulate the exposure of storage/caprock formations to the organic acid that is inherently present in the reservoir.^{20,24,33,38,48–50} However, the specific VOCs used to solubilize the organic acid could play a prominent role in the adsorption of organic acids on the rock surface, thereby determining the wettability of the rock surface and, hence, the quality of gas recovery, gas hydrate-based CO₂ capture and sequestration, and CO₂ containment security in the organic acid-contaminated formation.^{39,51–53}

In addition, the capacity of the rock to absorb fluids is influenced by its porosity. Previous research has shown that the presence of minute interstices (crevices) in which liquids can be stored can determine the extent of rock hydrophobicity or hydrophilicity.⁵⁴ Hence, a thorough understanding of the impacts of various solvents upon the adsorption of organics in both porous and non-porous rock is vital for evaluating the storage capacities and CO₂ containment safety of various organic acid-contaminated host rocks and for identifying the optimum conditions for risk-free geological CO₂ storage. In the present study, various solvents (deionized water, acetone, methanol, and *n*-decane) are used to prepare 10^{–2} mol/L stearic acid, and their effects on the adsorption coverage on porous and non-porous rocks are investigated. To determine the containment security of CO₂ in porous and non-porous sandstone formations, the contact angles of organic-aged and unaged quartz and Fontainebleau quartz are measured in CO₂/brine systems at various reservoir pressures of 0.1–20 MPa and temperatures of 298 and 323 K. The organic-aged Fontainebleau quartz is selected as an ideal representative of a simple natural porous sandstone formation, having a pure mineral composition of oxygen and silicon (99.5% quartz) with highly regular and uniform grains and pore framework.^{55–59} The clay composition of the Fontainebleau quartz is insignificant and does not play any prominent role.^{55–59} Thus, experiments

conducted with these samples can be easily repeated and reproduced in porous media. Nevertheless, the organic-acid contaminated geological storage formations must be appropriately simulated in order to assess the impact of organic acids on the CO₂ containment security in geo-storage formations.^{60,61} Unfortunately, there is a paucity of information in the literature on the impact of the base fluids upon the wettability (contact angle) of non-porous quartz and porous Fontainebleau quartz in CO₂/brine systems. Previously, silanes have been used as the conventional wettability alteration chemicals to achieve more hydrophobic conditions,^{40,41,62,63} but the actual geo-storage formations cannot be realistically aged with silanes due to their high reactivity.^{38,64,65} Hence, the contact angle measurements obtained herein for the Fontainebleau in CO₂-brine systems provide key insights into the wetting phenomenon of porous sandstone formations with uniform grain/pore sizes in the absence of clay minerals.

2. MATERIALS AND METHODS

The details of the materials used for the present study are presented in Table 1.

Table 1. Sources, Purity, and States of the Materials Used for the Present Study

material	source	purity	state
pure quartz	WARD'S Natural Science	99.9 mol %	solid
Fontainebleau	Cydarex	99.9 mol %	solid
acetone	Sigma-Aldrich/Rowe Scientific	99.9 mol %	liquid
methanol	Sigma-Aldrich/Rowe Scientific	99.9 mol %	liquid
<i>n</i> -decane	Chem-supply	99.9 mol %	liquid
NaCl	Chemlab	99.9 mol %	solid
KCl	Chemlab	99.9 mol %	solid
deionized water	David Gray	ultrapure	liquid
ultra-pure nitrogen	BOC Ltd Australia	99.999 wt %	gas
ultra-pure carbon dioxide	BOC Ltd Australia	99.999 wt %	gas
37.5% hydrochloric acid	Sigma-Aldrich	99%	aqueous

2.1. Aging Process with the Four Solutions. At realistic subsurface conditions, the geological storage formations are prone to the innate formation brines.^{60,61,66,67} Hence, to simulate the conventional storage formation, the quartz and Fontainebleau substrates were immersed in a representative formation brine solution (2% NaCl +1% KCl) for 30 min under ambient conditions.⁶⁸ The system acidity was maintained at pH 4 by the dropwise addition of aqueous hydrochloric acid. This ionizes the substrate surface and enhances the adsorption of organic acids, thereby simulating the anticipated contamination of geo-storage rocks by organic molecules due to millions of years of exposure.^{33,39,43,45,69–72}

To prepare the stearic acid solutions with a constant concentration (10^{–2} mol/L), the stearic acid powder was mixed with each solvent (deionized water, acetone, methanol, and *n*-decane) via magnetic stirring at 323 K for 30 min until the powder was fully dissolved. Subsequently, the quartz and Fontainebleau substrates were aged in various stearic acid/base solutions for 1 week to mimic the geological periods and conditions under which the geo-storage rocks are in contact with organic-acid containing formation fluids.^{1,33,39,69–71} The quartz and Fontainebleau substrate surfaces were then cleaned by applying ultra-pure N₂ to slough off the residual fluid from the surface of the substrates.³⁸

2.2. Characterization and Contact Angle Measurement. The surface roughness of the pure non-porous quartz and porous

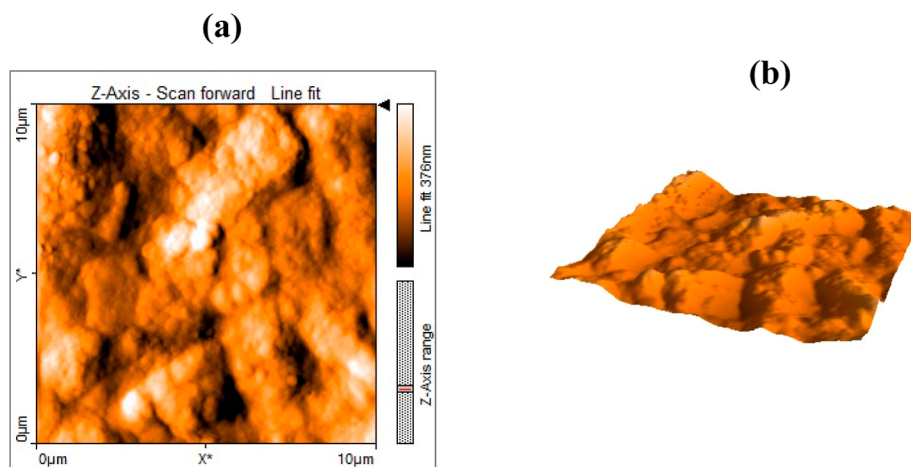


Figure 1. Surface morphology of the pure Fontainebleau quartz substrate: (a) 2D and (b) 3D.

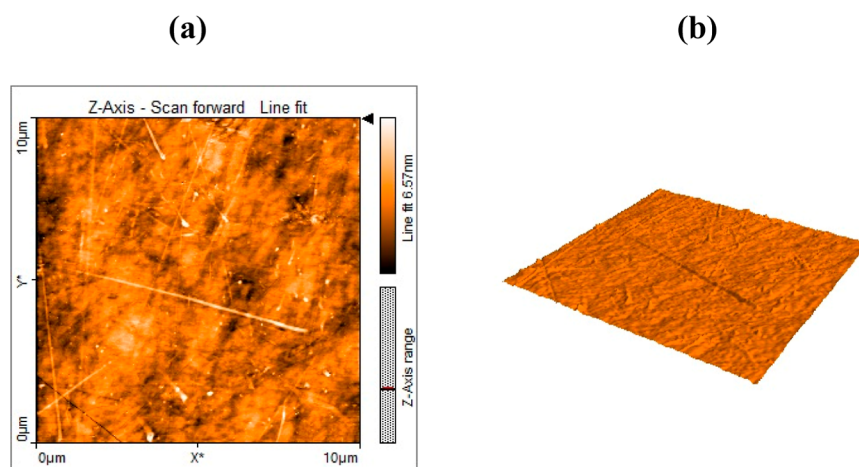


Figure 2. Surface morphology of the pure non-porous quartz substrate: (a) 2D and (b) 3D.

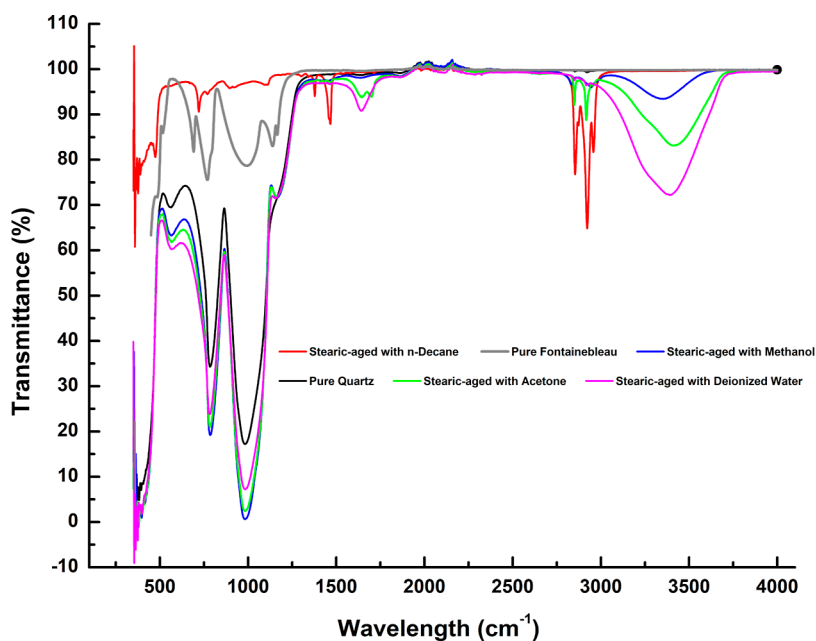


Figure 3. FTIR spectra of the pure and organic-aged non-porous quartz and Fontainebleau quartz.

Fontainebleau quartz were determined by atomic force microscopy (AFM; Flex-Axiom, Nanosurf with a C3000i controller). The extents

of stearic acid adsorption on the surfaces of the pure and aged substrates were examined via Fourier-transform infrared spectroscopy

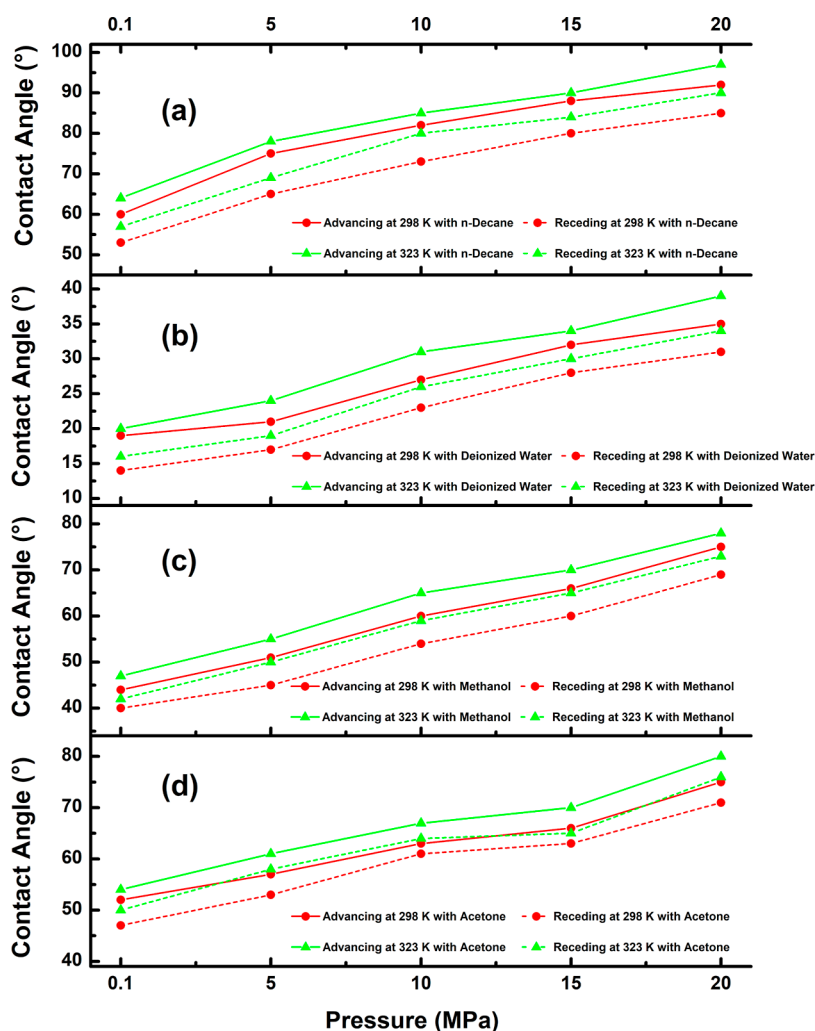


Figure 4. Measured contact angles of non-porous quartz treated with 10^{-2} mol/L solutions of stearic acid in (a) *n*-decane, (b) deionized water, (c) methanol, and (d) acetone at various pressures in the CO_2 /brine systems.

(FTIR; Perkin Elmer) in the spectral range of 400–4000 cm^{-1} for 64 scans.

The wettabilities of the quartz and Fontainebleau quartz in a brine/ CO_2 environment were determined via contact angle measurement, a popular method for evaluating the rock wetting phenomenon.^{23,26,38,40,47,73} The tilted plate method (17°) was used due to its versatility in assessing the advancing and receding angle simultaneously.⁷⁴ The measuring system consisted of a high-pressure-high-temperature cell connected to two Teledyne ISCO D-260 pumps for discharging the fluids into the system with a pressure accuracy of 0.01%.³⁸ To prevent mass transfer between the brine and CO_2 while measuring the contact angles, thermodynamic equilibration was ensured in a 500 mL Parr mixing reactor connected to a brine pump (ISCO) and CO_2 gas cylinder.⁷⁵ The brine salinity remained constant throughout the experimental matrix, at 2% NaCl + 1% KCl. Before dispersing CO_2 and brine into the system, the quartz or Fontainebleau sample was placed in the mixing reactor. The mixture was thoroughly stirred for 60 min at 1200 rpm to form a live brine at the desired temperature and pressure. The live brine was then transferred from the mixing reactor to the brine pump. After this, the aged quartz or Fontainebleau sample was positioned in a sample holder at a 17° tilt, the cell was firmly closed, and CO_2 was steadily injected to attain the desired experimental conditions. A heating bath (900 °F, Julabo), a heating controller (HTC101-002), and heating tape were used to maintain the temperature of the fluids in the ISCO pumps and the IFT cell. After the cell was filled with CO_2 under the selected experimental conditions, equilibrated brine with an average drop size

of $5 \pm 0.75 \mu\text{L}$ was introduced from the brine pump onto the surface of the titled quartz or Fontainebleau quartz slide using a high-accuracy pointer. The advancing and receding contact angles of the brine were then recorded at the leading and trailing edges of the droplet. The entire process was video-recorded using a high-performance video camera, and IMAGE J software was used to measure the contact angles from the images. A schematic diagram of the contact angle experimental setup is available in previous reports by the present authors.^{40,48}

3. RESULTS AND DISCUSSION

3.1. Surface Morphologies of the Pure and Organic-Aged Samples. The AFM results for the pure Fontainebleau quartz and the non-porous quartz substrates are presented in Figures 1 and 2, respectively. Here, the non-porous quartz has an average surface roughness of 6.57 nm, whereas that of the Fontainebleau quartz is 376 nm. These results indicate that the porous Fontainebleau quartz surface is much rougher than that of the non-porous quartz. Hence, pure Fontainebleau quartz is generally expected to demonstrate lower contact angles under hydrophilic conditions, or higher contact angles under hydrophobic conditions, with wider variations compared to the smoother surface of the pure non-porous quartz.^{50,76}

The FTIR results are presented in Figure 3, where the FTIR spectra of the pure non-porous quartz (black line) and the

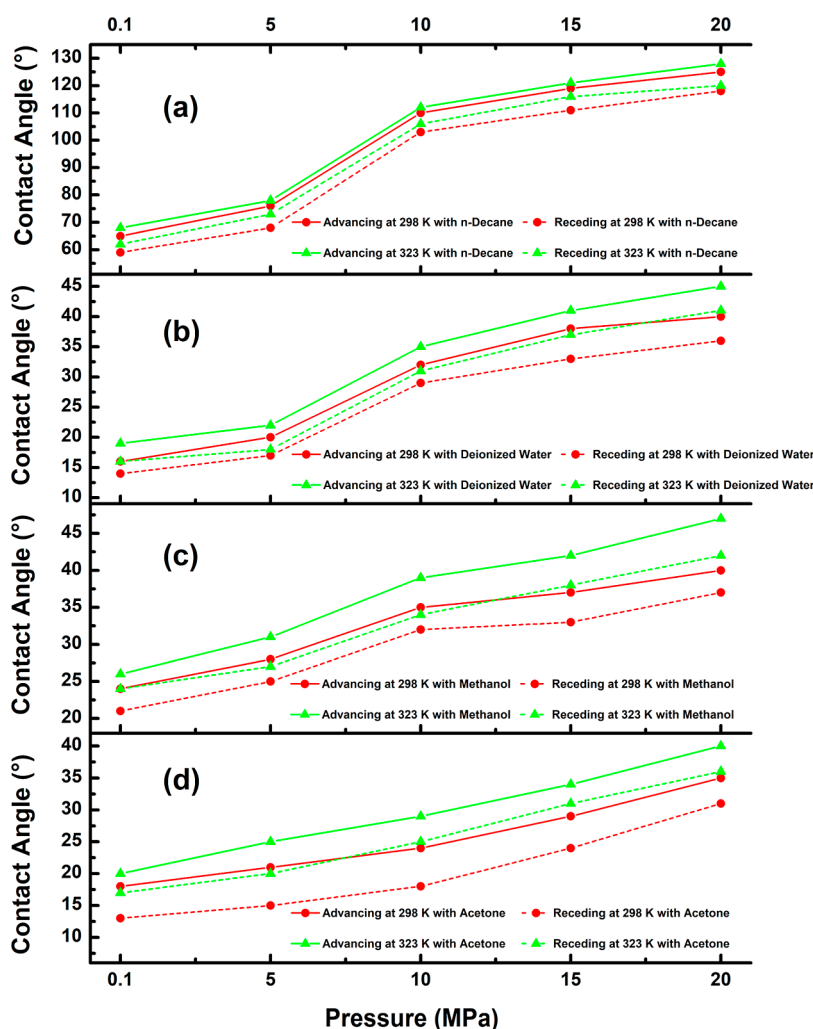


Figure 5. Measured contact angles of Fontainebleau quartz treated with 10^{-2} mol/L solutions of stearic acid in (a) *n*-decane, (b) deionized water, (c) methanol, and (d) acetone in the CO_2 /brine system.

pure Fontainebleau quartz (gray line) exhibit adsorption peaks at ~ 700 and 1100 cm^{-1} due to the Si–O asymmetric and symmetric bond vibrations, respectively. In addition, the asymmetric and symmetric bending vibrations of Si–O are observed at 450 and 650 cm^{-1} , thereby suggesting that the main content of the rock samples is silica. After aging in organic acids, the FTIR spectra exhibit similar trends of adsorption bands between 400 and 1100 cm^{-1} , but with additional sharp adsorption peaks between 2800 and 3600 cm^{-1} . In particular, the substrate aged in stearic acid/*n*-decane solution exhibits a sharp stretching doublet between 2840 and 2910 cm^{-1} due to the presence of hydrogen bonding (C–H) and hydroxyl bonding (C–OH). The FTIR spectra obtained before and after aging demonstrate that the hydroxyl groups on the quartz surface interact with those of the organic acids via covalent chemical bonding, which is responsible for hydrophobicity. This phenomenon is more pronounced when the quartz substrates are aged in stearic acid/*n*-decane solution than in the other solutions.

3.2. Effects of the Solvent on the CO_2 Wettability of Organic-Aged Porous and Nonporous Quartz Substrates. Stearic acid is a type of lipid, known as a fatty acid. Although the carboxyl end containing the two oxygen atoms is polar, the rest of the molecule is completely nonpolar, thereby

suggesting that stearic acids are fairly non-polar compounds, with little or no solubility in polar solvents such as methanol, acetone, and water. As noted above, several organic compounds have been used as base fluids for the preparation of various organic acid solutions in order to simulate the effect of organic acid contamination upon the wettability (contact angle) of rock in CO_2 /brine systems.^{39,47,51} The solvent that promotes the solubility of the organic acid will increase the adsorption of organic molecules onto the rock surface and, thus, exhibit contact angles greater than 90° . Conversely, the solvent that has a low tendency to promote the solubility and ionization process of the organic acid molecules may not provide the proper monolayer coverage responsible for the wettability modification.

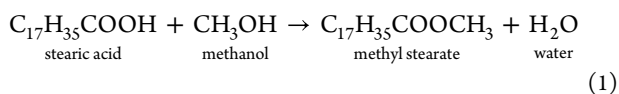
The CO_2 wettabilities (contact angles) of the quartz and Fontainebleau rocks before and after aging in acetone/stearic acid, methanol/stearic acid, deionized water/stearic acid, and *n*-decane/stearic acid solutions under various pressures and temperatures are presented in Figures 4 and 5, respectively. Before aging, the pure quartz is found to be water-wet, with advancing (θ_a) and receding (θ_r) contact angles of 51 and 44° , respectively, at an initial temperature of 298 K and an initial pressure of 0.1 MPa . Under similar thermo-physical conditions, the clean Fontainebleau quartz is also water-wet, with a lower

contact angle than that of pure quartz ($\theta_a = 30^\circ$, $\theta_r = 27^\circ$). After aging, the results show that the wettabilities of the quartz and Fontainebleau quartz are shifted increasingly toward the hydrophobic state as the pressure increases. Further, the comparative performances of the various solvents clearly indicate that *n*-decane is the most effective solvent for preparing the stearic acid to attain a fully CO₂-wetting state, as evidenced by the largest contact angle ranges in the top panels of Figures 4 and 5. Thus, at 20 MPa, the aging of the quartz surface in *n*-decane/stearic acid solution changes the wetting state of the pure quartz from water-wet ($\theta_a = 63^\circ$, $\theta_r = 57^\circ$) to the intermediate water-wetting conditions ($\theta_a = 92^\circ$, $\theta_r = 85^\circ$ at 298 K, and $\theta_a = 97^\circ$, $\theta_r = 90^\circ$ at 323 K; Figure 4a). At the same pressure, the *n*-decane/stearic acid solution alters the pure Fontainebleau quartz surface wettability from $\theta_a = 70^\circ$, $\theta_r = 65^\circ$ to a strongly CO₂-wet state, with $\theta_a = 125^\circ$ and $\theta_r = 118^\circ$ at 298 K, and $\theta_a = 128^\circ$, $\theta_r = 120^\circ$ at 323 K (Figure 5a). This trend is consistent with that observed in previous research, where the aging of rock surfaces in *n*-decane/stearic acid solution resulted in the attainment of intermediate water-wet and CO₂-wet conditions.^{20,33,34,77}

By contrast, when the quartz and Fontainebleau quartz surfaces are aged in acetone/stearic acid solution and methanol/stearic acid solution, the substrate surfaces are only altered into weakly water-wet conditions at the highest experimental temperature and pressure used herein (323 K and 20 MPa). Under those conditions, the presence of stearic acid/acetone shifts the advancing and receding contact angles of the non-porous quartz from $\theta_a = 67^\circ$ and $\theta_r = 61^\circ$ to $\theta_a = 80^\circ$ and $\theta_r = 76^\circ$ (Figure 4d). Similarly, the stearic acid/methanol solution shifts the contact angles of non-porous quartz to $\theta_a = 78^\circ$ and $\theta_r = 73^\circ$ under the same conditions (Figure 4c).

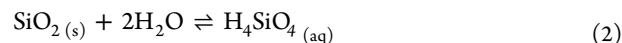
When the Fontainebleau quartz surfaces are aged with stearic acid in acetone and methanol solutions, the rock exhibits a mixed tendency in the brine/CO₂ system due to partial coverage by stearic acid. Particularly, at 0.1 MPa, the contact angle of the Fontainebleau quartz aged in stearic acid/acetone solution decreases from $\theta_a = 30^\circ$, $\theta_r = 27^\circ$ to $\theta_a = 18^\circ$, $\theta_r = 13^\circ$ at 298 K, and from $\theta_a = 33^\circ$, $\theta_r = 29^\circ$ to $\theta_a = 20^\circ$, $\theta_r = 17^\circ$ at 323 K (Figure 5d). At 20 MPa and 323 K, however, the advancing contact angle of the Fontainebleau quartz in the stearic acid/methanol solution decreases significantly from 74 to 47°, whereas the receding angle decreases from 69 to 42° (Figure 5c). Similar weakly water-wetting trends are observed for both the non-porous quartz (Figure 4b) and Fontainebleau quartz (Figure 5b) when deionized water is used as the solvent.

Generally, the contact angle measurements obtained herein clearly indicate that fully hydrophobic conditions are only attained when the rock substrate is aged in stearic acid/*n*-decane solution. The effectiveness of the selected solvent for the preparation of the desired concentration of stearic acid depends on the solubility of stearic acid in the respective solvent. Stearic acid comprises an 18 carbon-atom chain with a carboxylic acid group at one end (C₁₇H₃₅CO₂H). The reaction between stearic acid and methanol will produce methyl stearate and water, as shown in eq 1



The polar nature of the carboxyl end group suggests that the stearic acid could be soluble in the water/methanol solution due to the potential hydrogen bonding. However, the rest of

the molecule consists of a long hydrophobic hydrocarbon chain that repels water molecules, thereby rendering the stearic acid insoluble in polar solvents such as water, methanol, or acetone, and preventing the full adsorption of acid molecules on the non-porous quartz or Fontainebleau quartz surfaces. Moreover, partial dissolution of quartz in water may occur when the quartz or Fontainebleau surfaces are aged in water, methanol, or acetone solutions of stearic acid, thus resulting in the formation of silicic acid according to eq 2⁷⁸



However, the dissociation tendency of the stearic acid can only increase in the presence of a strong base, when a translucent solution is formed. In the presence of silicic acid, the solubility of stearic acid decreases in the basic solution, thereby increasing the surface hydrophobicity and further restricting the adsorption of stearic acid on the quartz and Fontainebleau quartz surfaces.

A previous study by Heryanto et al. (2007)⁷⁹ found that the solubility of stearic acid was the highest in the presence of ethyl acetate and lowest in the presence of methanol. In the present study, the solubility of stearic acid in the presence of the four organic solvents is found to decrease in the order: ethyl acetate > ethanol > acetone > methanol. This can be attributed to the hydrogen bonding properties and polarity of the system. In particular, the presence of hydrogen bonding increases the solubility and the ionization of the carboxylic acid group of the stearic acid in water.⁷⁹ Previous studies have also demonstrated that the polarity of stearic acid is very poor in polar solvents such as methanol and acetone compared to non-polar solvents such as *n*-decane. Beckmann et al.⁸⁰ observed that stearic acid dissolves almost entirely as dimers in *n*-decane, whereas a solvent–solute complex is formed after the dissolution of monomers when the stearic acid is dissolved in butanone under similar conditions. Thus, significant deviations from the ideal situation have been noticed when stearic acid is dissolved in methanol. Meanwhile, the favorable solubility behavior of stearic acid in *n*-decane relative to that in acetone, deionized water, and methanol has a profound impact on the adsorption of the organic acid on the quartz and Fontainebleau quartz surfaces. As a result, the stearic-acid solubilized carboxylic acid is chemisorbed at the quartz and Fontainebleau surfaces.^{1,33} Thus, when the substrate is aged in the stearic acid/*n*-decane solution, its surface becomes strongly hydrophobic due to the esterification reaction of the organic acid with the hydroxyl group of the mineral surface, thereby leading to covalent bonding.^{38,81} As a result, higher contact angles are measured for the aged quartz and Fontainebleau in the *n*-decane/stearic acid solution than in other solutions in the CO₂/brine system due to the higher coverage of the adsorbed organic acid molecules on the rock surfaces.

3.3. Influence of Temperature and Pressure on the CO₂ Wettability of Organic-Aged Porous and Non-porous Quartz Substrates. The results in Figures 4 and 5 clearly reveal the impact of temperature and pressure on the performance of the solvents used for the preparation of stearic acid. The contact angle is seen to increase with increasing temperature and pressure, thereby suggesting that the quartz and Fontainebleau will become more CO₂-wet (hydrophobic), and less water-wet (hydrophilic), as the storage formation becomes warmer and the CO₂ gas pressure increases. Similar results have been obtained for the wettability of quartz in

CO₂/brine systems³³ and H₂/brine environments.^{20,49} Generally, the density of CO₂ gas molecules increases with increasing pressure and, hence, the intermolecular interactions between the quartz/Fontainebleau quartz surfaces and the CO₂ gas molecules significantly increase at higher pressure, thereby creating hydrophobic surfaces.^{28,37,82} Moreover, although the decrease in gas density with increasing temperature has been found to result in lower contact angles and low CO₂-wettability of mica, calcite, and shale,^{28,36,82,83} the behavior of quartz is quite different. The contact angles of quartz rock in the CO₂/brine system are higher at higher temperatures because the surface hydrogen bonds between the silanol groups and water molecules are conveniently broken. This mechanism reduces the water wetting tendency and promotes the CO₂ wettability of the quartz and Fontainebleau quartz at high temperature, as observed in the present study.

3.4. CO₂ Wettability of the Unaged Porous and Nonporous Quartz Substrates. The CO₂ wettabilities of the pure porous Fontainebleau sandstones and pure non-porous quartz substrates are compared at various pressures of 0.1–20 MPa and temperatures of 298 and 323 K in Figure 6.

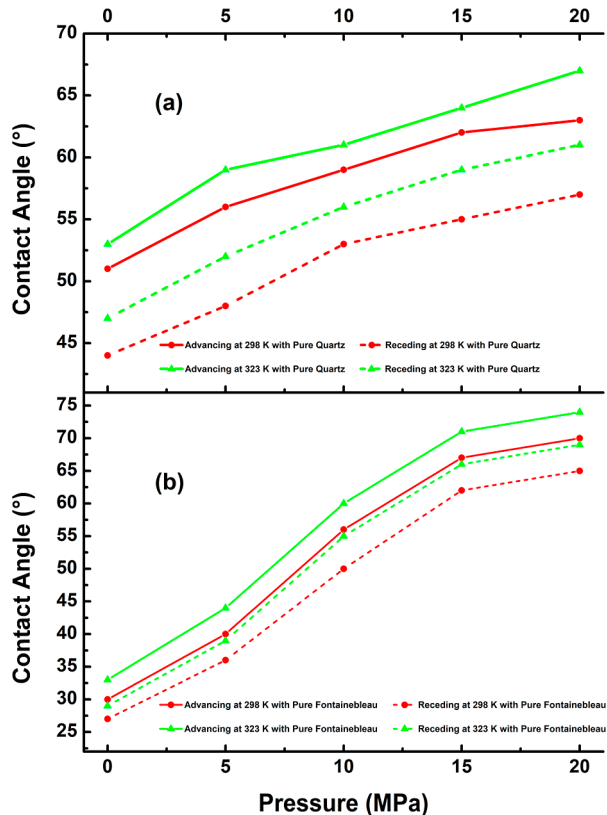


Figure 6. Measured contact angles of (a) unaged nonporous quartz and (b) porous Fontainebleau quartz at various pressures and temperatures.

Here, the contact angles are clearly seen to increase with increasing pressure and temperature, with the pure Fontainebleau quartz exhibiting a wider range of contact angles (27–74°) than the pure quartz (44–67°) under similar conditions. This is because the pore walls and crevices of the porous Fontainebleau quartz have a higher tendency to retain the stearic acid, thereby minimizing the entry of water into the smaller pores.^{35,84} Indeed, previous studies have shown that rougher surfaces are characterized by lower advancing and

receding contact angles in brine, as well as higher interfacial curvatures.^{55,85–87} Moreover, higher surface roughness correspond to progressively lower contact angles and narrower contact angle distributions.^{50,54,76} The lower contact angles of rougher surfaces have been attributed to water accumulation in surface crevices. This phenomenon discourages water dewetting of the surface, thus making it less prone to oil or gas wetting.^{55,85–87} The wide variations in the contact angles of rough surfaces are due to more deviations from the average (wider variations in local curvature) than for the smoother surfaces. Moreover, there is a considerable variation in the effective angle measured at the rough surface relative to the expected intrinsic local angle on the molecular scale.

In the pressure range of 0.1–10 MPa, the contact angles of the pure non-porous quartz are higher than those of the pure Fontainebleau at both 298 and 323 K. This is because the initial conditions are hydrophilic (water-wet), and the crevices of the porous Fontainebleau quartz are mainly filled with water. When the pressure is increased to 15 and 20 MPa, however, the contact angles of the Fontainebleau quartz are higher than those of the pure quartz. For instance, at 15 MPa and 298 K, the pure quartz has a θ_a of 62° and a θ_r of 55°, whereas the Fontainebleau has θ_a of 67° and a θ_r of 62°. When the temperature is raised to 323 K at the same pressure, the pure quartz has a θ_a of 64° and a θ_r of 59°, while the pure Fontainebleau has θ_a of 71° and a θ_r of 66°. Similar trends in the measured contact angles of pure quartz and pure Fontainebleau quartz are observed at 20 MPa. This is because the water that originally occupied the pores in the Fontainebleau quartz is replaced by CO₂ due to the increased CO₂ gas density and molecular interactions between the rock surface and the gas at higher pressures. These results support the previous assertion that variations in thermodynamic parameters, especially temperature and pressure, significantly influence the wetting behaviors of porous and non-porous quartz materials.^{50,84} Nevertheless, the larger range of contact angles observed for the porous Fontainebleau quartz relative to the non-porous quartz suggests that the surface roughness effects merely amplifies the inherent surface chemistry and original wetting state of the rock.⁵⁰

4. CONCLUSIONS

The wettability and interfacial tension between fluids and rock surfaces are fundamental properties that substantially influence the fluid flow, thermodynamics, storage capacities, and containment security.^{11,21,24–26,35,88–90} These properties are significantly influenced by the presence of inherent organic acids in geological storage formations.^{3,33,34,38,39} Previously, many studies have used various types of organic acids to simulate the real geological reservoir conditions on the laboratory scale.¹ Nevertheless, there is a serious lack of information regarding which solutions can provide suitable surface coverage and adsorption of such organic acids in representative porous and non-porous reservoir rocks. Hence, the present study was conducted in order to assess the impacts of various solutions on the adsorption of organics for porous and non-porous rock/CO₂/brine systems via contact angle measurements. The following conclusions were drawn:

1. The optimum adsorption of stearic acid on the rock surface to attain a fully hydrophobic state was achieved when *n*-decane was used as a solvent. By contrast, optimal adsorption was not achieved with acetone,

- deionized water, or methanol due to less than sufficient dissolution of stearic acid.
- The porous organic-aged Fontainebleau quartz exhibited higher contact angles than the non-porous organic-aged quartz due to higher adsorption and retention of organic molecules at the pore walls and crevices of the porous Fontainebleau quartz.
 - At pressures between 0.1 and 10 MPa, the unaged Fontainebleau surface demonstrated stronger water-wetting conditions, with a wider range of contact angles than that of the unaged non-porous quartz. This was attributed to the initial wetting conditions of the unaged Fontainebleau rock, wherein the crevices and smaller pore spaces are mainly filled with water.
 - When the pressure was increased to 15 and 20 MPa, higher contact angles were measured for the unaged Fontainebleau quartz than for the pure quartz. This was attributed to the increased CO₂ gas density and molecular interactions between the rock surfaces and CO₂ at higher pressures, which enabled the migration of more CO₂ into the pores that were originally occupied by water in porous Fontainebleau quartz.
 - The contact angles of both the organic-aged and unaged non-porous quartz and porous Fontainebleau quartz increased with increasing pressure and temperature.

In brief, these results provide a fundamental understanding of how various parameters, including pressure, temperature, and surface roughness, along with the presence of organic acids and their preparation with various solvents, affect the wetting characteristics of porous and non-porous geological storage rocks. Future reservoir models should consider these parameters and their effects in order to accurately calculate the CO₂ geo-storage capacities and thereby reduce the uncertainties in the feasibility of large-scale CO₂ geological storage projects.

AUTHOR INFORMATION

Corresponding Authors

Muhammad Ali – Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia; School of Engineering, Edith Cowan University, Joondalup 6027 Western Australia, Australia; orcid.org/0000-0002-2446-3072; Email: Mhammad.ali.2@kaust.edu.sa

Hussein Hoteit – Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia; orcid.org/0000-0002-3900-7272; Email: Hussein.hoteit@kaust.edu.sa

Authors

Nurudeen Yekeen – Department of Chemical & Petroleum Engineering, Faculty of Engineering, Technology and Built Environment, UCSI University, 56000 Kuala Lumpur, Malaysia

Mujahid Ali – School of Engineering, Edith Cowan University, Joondalup 6027 Western Australia, Australia

Mirhasan Hosseini – School of Engineering, Edith Cowan University, Joondalup 6027 Western Australia, Australia; orcid.org/0000-0001-6400-0366

Nilanjan Pal – Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia; Department of Petroleum

Engineering, Indian Institute of Petroleum and Energy, Visakhapatnam 530003, India; orcid.org/0000-0002-1892-9745

Alireza Keshavarz – School of Engineering, Edith Cowan University, Joondalup 6027 Western Australia, Australia; orcid.org/0000-0002-8091-961X

Stefan Iglauer – School of Engineering, Edith Cowan University, Joondalup 6027 Western Australia, Australia; orcid.org/0000-0002-8080-1590

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.energyfuels.2c01696>

Notes

The authors declare no competing financial interest.

REFERENCES

- Ali, M.; Jha, N. K.; Pal, N.; Keshavarz, A.; Hoteit, H.; Sarmadivaleh, M. Recent advances in carbon dioxide geological storage, experimental procedures, influencing parameters, and future outlook. *Earth-Sci. Rev.* **2021**, *225*, 103895.
- Ali, M. Effect of Organic Surface Concentration on CO₂-Wettability of Reservoir Rock. Master of Philosophy thesis, Curtin University, 2018.
- Ali, M. Effect of Organics and Nanoparticles on CO₂-Wettability of Reservoir Rock; Implications for CO₂ Geo-Storage. Doctor of Philosophy thesis, Curtin University, 2021.
- Orr, F. M. Onshore geologic storage of CO₂. *Science* **2009**, *325*, 1656–1658.
- Blunt, M.; Fayers, F. J., Jr.; Orr, F. M. Carbon dioxide in enhanced oil recovery. *Energy Convers. Manage.* **1993**, *34*, 1197–1204.
- Bui, M.; Adjiman, C. S.; Bardow, A.; Anthony, E. J.; Boston, A.; Brown, S.; Fennell, P. S.; Fuss, S.; Galindo, A.; Hackett, L. A.; Hallett, J. P.; Herzog, H. J.; Jackson, G.; Kemper, J.; Krevor, S.; Maitland, G. C.; Matuszewski, M.; Metcalfe, I. S.; Petit, C.; Puxty, G.; Reimer, J.; Reiner, D. M.; Rubin, E. S.; Scott, S. A.; Shah, N.; Smit, B.; Trusler, J. P. M.; Webley, P.; Wilcox, J.; Mac Dowell, N. Carbon capture and storage (CCS): the way forward. *Energy Environ. Sci.* **2018**, *11*, 1062–1176.
- Hosseini, M.; Ali, M.; Fahimpour, J.; Keshavarz, A.; Iglauer, S. Assessment of rock-hydrogen and rock-water interfacial tension in shale, evaporite and basaltic rocks. *Journal of Natural Gas Science and Engineering* **2022**, 104743.
- Hassanpouryouzband, A.; Adie, K.; Cowen, T.; Thaysen, E. M.; Heinemann, N.; Butler, I. B.; Wilkinson, M.; Edlmann, K. Geological Hydrogen Storage: Geochemical Reactivity of Hydrogen with Sandstone Reservoirs. *ACS Energy Lett.* **2022**, *7*, 2203–2210.
- Hassanpouryouzband, A.; Joonaki, E.; Edlmann, K.; Haszeldine, R. S. Offshore geological storage of hydrogen: Is this our best option to achieve net-zero? *ACS Energy Lett.* **2021**, *6*, 2181–2186.
- Mohanty, U. S.; Ali, M.; Azhar, M. R.; Al-Yaseri, A.; Keshavarz, A.; Iglauer, S. Current advances in syngas (CO+ H₂) production through bi-reforming of methane using various catalysts: A review. *Int. J. Hydrogen Energy* **2021**, *46*, 32809.
- Hosseini, M.; Fahimpour, J.; Ali, M.; Keshavarz, A.; Iglauer, S. H₂– brine interfacial tension as a function of salinity, temperature, and pressure; implications for hydrogen geo-storage. *J. Pet. Sci. Eng.* **2022**, *213*, 110441.
- Yekeen, N.; Al-Yaseri, A.; Negash, B. M.; Ali, M.; Giwelli, A.; Esteban, L.; Sarout, J. Clay-hydrogen and clay-cushion gas interfacial tensions: Implications for hydrogen storage. *Int. J. Hydrogen Energy* **2022**, *47*, 19155–19167.
- Alanazi, A.; Bawazeer, S.; Ali, M.; Keshavarz, A.; Hoteit, H. Thermodynamic modeling of hydrogen–water systems with gas impurity at various conditions using cubic and PC-SAFT equations of state. *Energy Convers. Manage.: X* **2022**, *15*, 100257.
- Awan, F. U. R.; Keshavarz, A.; Azhar, M. R.; Akhondzadeh, H.; Ali, M.; Al-Yaseri, A.; Abid, H. R.; Iglauer, S. Adsorption of

nanoparticles on glass bead surface for enhancing proppant performance: A systematic experimental study. *J. Mol. Liq.* **2021**, *328*, 115398.

(15) Clark, M. A.; Domingo, N. G.; Colgan, K.; Thakrar, S. K.; Tilman, D.; Lynch, J.; Azevedo, I. L.; Hill, J. D. Global food system emissions could preclude achieving the 1.5 and 2 C climate change targets. *Science* **2020**, *370*, 705–708.

(16) O'Brien, K. Is the 1.5 C target possible? Exploring the three spheres of transformation. *Curr. Opin. Environ. Sustain.* **2018**, *31*, 153–160.

(17) Al-Yaseri, A.; Yekeen, N.; Ali, M.; Pal, N.; Verma, A.; Abdulelah, H.; Hoteit, H.; Sarmadivaleh, M. Effect of organic acids on CO₂-rock and water-rock interfacial tension: Implications for CO₂ geo-storage. *J. Pet. Sci. Eng.* **2022**, *214*, 110480.

(18) Iglauer, S.; Akhondzadeh, H.; Abid, H.; Paluszny, A.; Keshavarz, A.; Ali, M.; Giwelli, A.; Esteban, L.; Sarout, J.; Lebedev, M. Hydrogen flooding of a coal core: effect on coal swelling. *Geophys. Res. Lett.* **2022**, *49*, No. e2021GL096873.

(19) Iglauer, S.; Ali, M.; Keshavarz, A. Hydrogen Wettability of Sandstone Reservoirs: Implications for Hydrogen Geo-Storage. *Geophys. Res. Lett.* **2021**, *48*, No. e2020GL090814.

(20) Ali, M.; Jha, N. K.; Al-Yaseri, A.; Zhang, Y.; Iglauer, S.; Sarmadivaleh, M. Hydrogen wettability of quartz substrates exposed to organic acids; Implications for hydrogen trapping/storage in sandstone reservoirs. *J. Pet. Sci. Eng.* **2021**, *207*, 109081.

(21) Ali, M.; Pan, B.; Yekeen, N.; Al-Anssari, S.; Al-Anazi, A.; Keshavarz, A.; Iglauer, S.; Hoteit, H. Assessment of wettability and rock-fluid interfacial tension of caprock: Implications for hydrogen and carbon dioxide geo-storage. *Int. J. Hydrogen Energy* **2022**, *47*, 14104.

(22) Arif, M.; Abu-Khamsin, S.; Iglauer, S. Wettability of rock/CO₂/brine and rock/oil/CO₂-enriched-brine systems: Critical parametric analysis and future outlook. *Adv. Colloid Interface Sci.* **2019**, *268*, 91.

(23) Arif, M.; Barifcani, A.; Lebedev, M.; Iglauer, S. Structural trapping capacity of oil-wet caprock as a function of pressure, temperature and salinity. *Int. J. Greenhouse Gas Control* **2016**, *50*, 112–120.

(24) Hosseini, M.; Fahimpour, J.; Ali, M.; Keshavarz, A.; Iglauer, S. Capillary Sealing Efficiency Analysis of Caprocks: Implication for Hydrogen Geological Storage. *Energy Fuels* **2022**, *36*, 4065.

(25) Iglauer, S. CO₂-water-rock wettability: variability, influencing factors, and implications for CO₂ geostorage. *Acc. Chem. Res.* **2017**, *50*, 1134–1142.

(26) Iglauer, S.; Pentland, C.; Busch, A. CO₂ wettability of seal and reservoir rocks and the implications for carbon geo-sequestration. *Water Resour. Res.* **2015**, *51*, 729–774.

(27) Pal, N.; Zhang, X.; Ali, M.; Mandal, A.; Hoteit, H. Carbon dioxide thickening: A review of technological aspects, advances and challenges for oilfield application. *Fuel* **2022**, *315*, 122947.

(28) Yekeen, N.; Padmanabhan, E.; Sevo, A.; Kanesen, L.; Okunade, A.; Kanesen, L.; Okunade, O. A. Wettability of rock/CO₂/brine systems: A critical review of influencing parameters and recent advances. *J. Ind. Eng. Chem.* **2020**, *88*, 1–28.

(29) Al-Anssari, S.; Arain, Z.-U.-A.; Barifcani, A.; Keshavarz, A.; Ali, M.; Iglauer, S. In Influence of Pressure and Temperature on CO₂-Nanofluid Interfacial Tension: Implication for Enhanced Oil Recovery and Carbon Geosequestration. *Abu Dhabi International Petroleum Exhibition & Conference*; Society of Petroleum Engineers, 2018.

(30) Jha, N. K.; Ali, M.; Iglauer, S.; Lebedev, M.; Roshan, H.; Barifcani, A.; Sangwai, J. S.; Sarmadivaleh, M. Wettability alteration of quartz surface by low-salinity surfactant nanofluids at high-pressure and high-temperature conditions. *Energy Fuels* **2019**, *33*, 7062–7068.

(31) Memon, S.; Feng, R.; Ali, M.; Bhatti, M. A.; Giwelli, A.; Keshavarz, A.; Xie, Q.; Sarmadivaleh, M. Supercritical CO₂-Shale interaction induced natural fracture closure: Implications for scCO₂ hydraulic fracturing in shales. *Fuel* **2021**, *313*, 122682.

(32) Abdulelah, H.; Al-Yaseri, A.; Ali, M.; Giwelli, A.; Negash, B. M.; Sarmadivaleh, M. CO₂/Basalt's interfacial tension and wettability

directly from gas density: Implications for Carbon Geo-sequestration. *J. Pet. Sci. Eng.* **2021**, *204*, 108683.

(33) Ali, M.; Arif, M.; Sahito, M. F.; Al-Anssari, S.; Keshavarz, A.; Barifcani, A.; Stalker, L.; Sarmadivaleh, M.; Iglauer, S. CO₂-wettability of sandstones exposed to traces of organic acids: Implications for CO₂ geo-storage. *Int. J. Greenhouse Gas Control* **2019**, *83*, 61–68.

(34) Ali, M.; Awan, F. U. R.; Ali, M.; Al-Yaseri, A.; Arif, M.; Sánchez-Román, M.; Keshavarz, A.; Iglauer, S. Effect of humic acid on CO₂-wettability in sandstone formation. *J. Colloid Interface Sci.* **2021**, *588*, 315–325.

(35) Al-Yaseri, A.; Roshan, H.; Zhang, Y.; Rahman, T.; Lebedev, M.; Barifcani, A.; Iglauer, S. Effect of the temperature on CO₂/brine/dolomite wettability: hydrophilic versus hydrophobic surfaces. *Energy Fuels* **2017**, *31*, 6329–6333.

(36) Yekeen, N.; Padmanabhan, E.; Abdulelah, H.; Irfan, S. A.; Okunade, O. A.; Khan, J. A.; Negash, B. M. CO₂/brine interfacial tension and rock wettability at reservoir conditions: A critical review of previous studies and case study of black shale from Malaysian formation. *J. Pet. Sci. Eng.* **2021**, *196*, 107673.

(37) Al-Yaseri, A.; Ali, M.; Ali, M.; Taheri, R.; Wolff-Boenisch, D. Western Australia basalt-CO₂-brine wettability at geo-storage conditions. *J. Colloid Interface Sci.* **2021**, *603*, 165–171.

(38) Ali, M.; Aftab, A.; Arain, Z.-U.-A.; Al-Yaseri, A.; Roshan, H.; Saeedi, A.; Iglauer, S.; Sarmadivaleh, M. Influence of organic acid concentration on wettability alteration of cap-rock: implications for CO₂ trapping/storage. *ACS Appl. Mater. Interfaces* **2020**, *12*, 39850–39858.

(39) Ali, M.; Al-Anssari, S.; Arif, M.; Barifcani, A.; Sarmadivaleh, M.; Stalker, L.; Lebedev, M.; Iglauer, S. Organic acid concentration thresholds for ageing of carbonate minerals: Implications for CO₂ trapping/storage. *J. Colloid Interface Sci.* **2019**, *534*, 88–94.

(40) Ali, M.; Aftab, A.; Awan, F. U. R.; Akhondzadeh, H.; Keshavarz, A.; Saeedi, A.; Iglauer, S.; Sarmadivaleh, M. CO₂-wettability reversal of cap-rock by alumina nanofluid: Implications for CO₂ geo-storage. *Fuel Process. Technol.* **2021**, *214*, 106722.

(41) Ali, M.; Sahito, M. F.; Jha, N. K.; Arain, S.; Memon, A.; Keshavarz, S.; Iglauer, S.; Saeedi, M.; Sarmadivaleh, M. Effect of nanofluid on CO₂-wettability reversal of sandstone formation; implications for CO₂ geo-storage. *J. Colloid Interface Sci.* **2020**, *559*, 304–312.

(42) Jones, D.; Head, I.; Gray, N.; Adams, J.; Rowan, A.; Aitken, C.; Bennett, B.; Huang, H.; Brown, A.; Bowler, B.; Oldenburg, T.; Erdmann, M.; Larter, S. R. Crude-oil biodegradation via methanogenesis in subsurface petroleum reservoirs. *Nature* **2008**, *451*, 176–180.

(43) Akob, D. M.; Cozzarelli, I. M.; Dunlap, D. S.; Rowan, E. L.; Lorah, M. M. Organic and inorganic composition and microbiology of produced waters from Pennsylvania shale gas wells. *Appl. Geochem.* **2015**, *60*, 116–125.

(44) Kvenvolden, K. A. Normal fatty acids in sediments. *J. Am. Oil Chem. Soc.* **1967**, *44*, 628–636.

(45) Lundegard, P. D.; Kharaka, Y. K. Distribution and occurrence of organic acids in subsurface waters. *Organic Acids in Geological Processes*; Springer, 1994; pp 40–69.

(46) Caballero, B.; Trugo, L. C.; Finglas, P. M. *Encyclopedia of Food Sciences and Nutrition*; Academic, 2003.

(47) Al-Anssari, S.; Barifcani, A.; Wang, S.; Maxim, L.; Iglauer, S. Wettability alteration of oil-wet carbonate by silica nanofluid. *J. Colloid Interface Sci.* **2016**, *461*, 435–442.

(48) Ali, M.; Yekeen, N.; Pal, N.; Keshavarz, A.; Iglauer, S.; Hoteit, H. Influence of organic molecules on wetting characteristics of mica/H₂O/brine systems: Implications for hydrogen structural trapping capacities. *J. Colloid Interface Sci.* **2022**, *608*, 1739–1749.

(49) Ali, M.; Yekeen, N.; Pal, N.; Keshavarz, A.; Iglauer, S.; Hoteit, H. Influence of pressure, temperature and organic surface concentration on hydrogen wettability of caprock; implications for hydrogen geo-storage. *Energy Rep.* **2021**, *7*, 5988–5996.

- (50) Hosseini, M.; Fahimpour, J.; Ali, M.; Keshavarz, A.; Iglauer, S. Hydrogen wettability of carbonate formations: Implications for hydrogen geo-storage. *J. Colloid Interface Sci.* **2022**, *614*, 256.
- (51) Al-Anssari, S.; Arif, M.; Wang, S.; Barifcani, A.; Lebedev, M.; Iglauer, S. Wettability of nanofluid-modified oil-wet calcite at reservoir conditions. *Fuel* **2018**, *211*, 405–414.
- (52) Hu, W.; Chen, C.; Sun, J.; Zhang, N.; Zhao, J.; Liu, Y.; Ling, Z.; Li, W.; Liu, W.; Song, Y. Three-body aggregation of guest molecules as a key step in methane hydrate nucleation and growth. *Commun. Chem.* **2022**, *5*, 33.
- (53) Sun, J.; Chen, C.; Zhang, Y.; Li, W.; Song, Y. Competitive adsorption characteristics based on partial pressure and adsorption mechanism of CO₂/CH₄ mixture in shale pores. *Chem. Eng. J.* **2022**, *430*, 133172.
- (54) Marmur, A. Soft contact: measurement and interpretation of contact angles. *Soft Matter* **2006**, *2*, 12–17.
- (55) Reviron, N.; Reuschlé, T.; Bernard, J.-D. The brittle deformation regime of water-saturated siliceous sandstones. *Geophys. J. Int.* **2009**, *178*, 1766–1778.
- (56) Haddad, S. C.; Worden, R. H.; Prior, D. J.; Smalley, P. C. Quartz Cement in the Fontainebleau Sandstone, Paris Basin, France: crystallography and implications for mechanisms of cement growth. *J. Sediment. Res.* **2006**, *76*, 244–256.
- (57) Al Saadi, F.; Wolf, K.; Kruijsdijk, C. Characterization of Fontainebleau sandstone: quartz overgrowth and its impact on pore-throat framework. *J. Pet. Environ. Biotechnol.* **2017**, *7*, 1–12.
- (58) Walderhaug, O.; Eliassen, A.; Aase, N. E. Prediction of permeability in quartz-rich sandstones: examples from the Norwegian continental shelf and the Fontainebleau sandstone. *J. Sediment. Res.* **2012**, *82*, 899–912.
- (59) Kreutzer, S.; Friedrich, J.; Sanderson, D.; Adamiec, G.; Chruścińska, A.; Fasoli, M.; Martini, M.; Polymeris, G.; Burbidge, C.; Schmidt, C. Les sables de fontainebleau: a natural quartz reference sample and its characterisation. *Ancient TL* **2017**, *35*, 21.
- (60) Davis, J. A. Adsorption of natural dissolved organic matter at the oxide/water interface. *Geochim. Cosmochim. Acta* **1982**, *46*, 2381–2393.
- (61) Kleber, M.; Eusterhues, K.; Keiluweit, M.; Mikutta, C.; Mikutta, R.; Nico, P. S., Mineral–organic associations: formation, properties, and relevance in soil environments. In *Adv. Agron.*, Elsevier: 2015; Vol. 130, pp 1–140. DOI: 10.1016/bs.agron.2014.10.005
- (62) Al-Anssari, S.; Arif, M.; Wang, S.; Barifcani, A.; Lebedev, M.; Iglauer, S. CO₂ geo-storage capacity enhancement via nanofluid priming. *Int. J. Greenhouse Gas Control* **2017**, *63*, 20–25.
- (63) Al-Yaseri, A.; Ali, M.; Abbasi, G. R.; Abid, H. R.; Jha, N. K. Enhancing CO₂ storage capacity and containment security of basaltic formation using silica nanofluids. *Int. J. Greenhouse Gas Control* **2021**, *112*, 103516.
- (64) Grate, J. W.; Dehoff, K. J.; Warner, M. G.; Pittman, J. W.; Wietsma, T. W.; Zhang, C.; Oostrom, M. Correlation of oil–water and air–water contact angles of diverse silanized surfaces and relationship to fluid interfacial tensions. *Langmuir* **2012**, *28*, 7182–7188.
- (65) Bennett, P.; Siegel, D.; Baedecker, M. J.; MF, M. Crude oil in a shallow sand and gravel aquifer—I. Hydrogeology and inorganic geochemistry. *Appl. Geochem.* **1993**, *8*, 529–549.
- (66) Ulrich, H. J.; Stumm, W.; Cosovic, B. Adsorption of aliphatic fatty acids on aquatic interfaces. Comparison between two model surfaces: the mercury electrode and δ -Al₂O₃ colloids. *Environ. Sci. Technol.* **1988**, *22*, 37–41.
- (67) Zullig, J. J.; Morse, J. W. Interaction of organic acids with carbonate mineral surfaces in seawater and related solutions: I. Fatty acid adsorption. *Geochim. Cosmochim. Acta* **1988**, *52*, 1667–1678.
- (68) Esfandiyari, H.; Sarmadivaleh, M.; Esmailzadeh, F.; Ali, M.; Iglauer, S.; Keshavarz, A. Experimental evaluation of rock mineralogy on hydrogen-wettability: Implications for hydrogen geo-storage. *J. Energy Storage* **2022**, *52*, 104866.
- (69) Jardine, P.; McCarthy, J.; Weber, N. Mechanisms of dissolved organic carbon adsorption on soil. *Soil Sci. Soc. Am. J.* **1989**, *53*, 1378–1385.
- (70) Stalker, L.; Varma, S.; Van Gent, D.; Haworth, J.; Sharma, S. South West Hub: a carbon capture and storage project. *Aust. J. Earth Sci.* **2013**, *60*, 45–58.
- (71) Madsen, L.; Lind, L. Adsorption of carboxylic acids on reservoir minerals from organic and aqueous phase. *SPE Reservoir Eval. Eng.* **1998**, *1*, 47–51.
- (72) Arain, Z.-U.-A.; Al-Anssari, S.; Ali, M.; Memon, S.; Bhatti, M. A.; Lagat, C.; Sarmadivaleh, M. Reversible and irreversible adsorption of bare and hybrid silica nanoparticles onto carbonate surface at reservoir condition. *Petroleum* **2019**, *6*, 277.
- (73) Iglauer, S.; Al-Yaseri, A. Z.; Rezaee, R.; Lebedev, M. CO₂ wettability of caprocks: Implications for structural storage capacity and containment security. *Geophys. Res. Lett.* **2015**, *42*, 9279–9284.
- (74) Lander, L. M.; Siewierski, L. M.; Brittain, W. J.; Vogler, E. A. A systematic comparison of contact angle methods. *Langmuir* **1993**, *9*, 2237–2239.
- (75) El-Maghraby, R.; Pentland, C.; Iglauer, S.; Blunt, M. A fast method to equilibrate carbon dioxide with brine at high pressure and elevated temperature including solubility measurements. *J. Supercrit. Fluids* **2012**, *62*, 55–59.
- (76) Al-Yaseri, A. Z.; Lebedev, M.; Barifcani, A.; Iglauer, S. Receding and advancing (CO₂+ brine+ quartz) contact angles as a function of pressure, temperature, surface roughness, salt type and salinity. *J. Chem. Thermodyn.* **2016**, *93*, 416–423.
- (77) Ali, M.; Arif, M.; Sánchez-Román, M.; Keshavarz, A.; Iglauer, S. Influence of Humic acids on CO₂-quartz wettability: Implications for CO₂ storage. *Proceedings of the 15th Greenhouse Gas Control Technologies Conference 15–18 March* Available at SSRN 3815420, 2021.
- (78) Crundwell, F. K. On the mechanism of the dissolution of quartz and silica in aqueous solutions. *ACS Omega* **2017**, *2*, 1116–1127.
- (79) Heryanto, R.; Hasan, M.; Abdullah, E. C.; Kumoro, A. C. Solubility of stearic acid in various organic solvents and its prediction using non-ideal solution models. *ScienceAsia* **2007**, *33*, 469–472.
- (80) Beckmann, W.; Boistelle, R.; Sato, K. Solubility of the A, B, and C polymorphs of stearic acid in decane, methanol, and butanone. *J. Chem. Eng. Data* **1984**, *29*, 211–214.
- (81) Al-Balushi, M. A.; Karimi, M.; Al-Maamari, R. S. Impact of acid and base numbers and their ratios on wettability alteration of the calcite surface. *Energy Fuels* **2019**, *34*, 245–257.
- (82) Arif, M.; Abu-Khamsin, S. A.; Iglauer, S. Wettability of rock/CO₂/brine and rock/oil/CO₂-enriched-brine systems: Critical parametric analysis and future outlook. *Adv. Colloid Interface Sci.* **2019**, *268*, 91–113.
- (83) Arif, M.; Zhang, Y.; Iglauer, S. Shale wettability: Data sets, challenges, and outlook. *Energy Fuels* **2021**, *35*, 2965–2980.
- (84) Alnili, F.; Al-Yaseri, A.; Roshan, H.; Rahman, T.; Verall, M.; Lebedev, M.; Sarmadivaleh, M.; Iglauer, S.; Barifcani, A. Carbon dioxide/brine wettability of porous sandstone versus solid quartz: An experimental and theoretical investigation. *J. Colloid Interface Sci.* **2018**, *524*, 188–194.
- (85) AlRatrou, A.; Blunt, M. J.; Bijeljic, B. Wettability in complex porous materials, the mixed-wet state, and its relationship to surface roughness. *Proc. Natl. Acad. Sci. U.S.A.* **2018**, *115*, 8901–8906.
- (86) Cassie, A.; Baxter, S. Wettability of porous surfaces. *Trans. Faraday Soc.* **1944**, *40*, 546–551.
- (87) Gu, H.; Wang, C.; Gong, S.; Mei, Y.; Li, H.; Ma, W. Investigation on contact angle measurement methods and wettability transition of porous surfaces. *Surf. Coat. Technol.* **2016**, *292*, 72–77.
- (88) Al-Khdheawi, E. A.; Mahdi, D. S.; Ali, M.; Iglauer, S.; Barifcani, A. Reservoir Scale Porosity-Permeability Evolution in Sandstone Due to CO₂ Geological Storage. *Proceedings of the 15th Greenhouse Gas Control Technologies Conference 15–18 March* Available at SSRN 3818887, 2021.
- (89) Al-Khdheawi, E. A.; Vialle, S.; Barifcani, A.; Sarmadivaleh, M.; Iglauer, S. Impact of reservoir wettability and heterogeneity on CO₂-

plume migration and trapping capacity. *Int. J. Greenhouse Gas Control* **2017**, *58*, 142–158.

(90) Arif, M.; Abu-Khamsin, S. A.; Zhang, Y.; Iglauer, S. Experimental investigation of carbonate wettability as a function of mineralogical and thermo-physical conditions. *Fuel* **2020**, *264*, 116846.

NOTE ADDED AFTER ASAP PUBLICATION

This paper was published ASAP on August 26, 2022 with an error in the title. The corrected version was reposted on August 29, 2022.

Recommended by ACS

DLVO-Based Analyses of the Water Vapor Adsorption and Condensation in Hydrophilic Nanopores of Low-Rank Coal

Hao Wu, Yanhai Chang, *et al.*

JULY 08, 2021
ENERGY & FUELS

READ 

CO₂-Brine Contact Angle Measurements on Navajo, Nugget, Bentheimer, Bandera Brown, Berea, and Mt. Simon Sandstones

Foad Haeri, Angela Goodman, *et al.*

APRIL 06, 2020
ENERGY & FUELS

READ 

Numerical Simulation of CO₂ Huff and Puff Feasibility for Light Oil Reservoirs in the Appalachian Basin: Sensitivity Study and History Match of a CO₂ Pilot Test

Samin Raziperchikolaee and Srikanta Mishra

OCTOBER 14, 2019
ENERGY & FUELS

READ 

Molecular Dynamics Study on CO₂ Storage in Water-Filled Kerogen Nanopores in Shale Reservoirs: Effects of Kerogen Maturity and Pore Size

Wenhui Li, Zhehui Jin, *et al.*

DECEMBER 21, 2020
LANGMUIR

READ 

Get More Suggestions >