Natural Gas Storage on Nanoporous Carbon

Jacob Burress, Mikael Wood, Sarah Barker, John Flavin, Cintia Lapilli, Parag Shah, Galen Suppes, Peter Pfeifer

Alliance for Collaborative Research in Alternative Fuel Technology

University of Missouri, Columbia, MO 65211
Overview

- Powdered and monolithic activated carbons have been made with corn cob as starting material that have a large methane storage capacity.
- Pore Space Structure Analyzed:
  - small angle x-ray scattering (SAXS)
  - computer simulations of pore formation
  - nitrogen adsorption isotherms
  - scanning and transmission electron microscopy (SEM/TEM)
  - methane adsorption isotherms
Why are Nanopores Important?

- In narrow pores, van der Waals potentials overlap; creating a deep energy well
  - Max. CH$_4$ capacity in pores of width 1.1 nm (simulations)
- van der Waals potential of CH$_4$ in pore of width 1.1 nm
- Energy loss more than enough to compress CH$_4$ into dense fluid; remaining energy $\rightarrow$ heat


Binding energy: 17 kJ/mol
Why are Nanopores Important?

- Width ~3.7 Å
- Width ~6 Å
- Width ~11 Å
- Width ~22 Å
Definitions of Uptake Values

\[ m_{\text{absolute adsorbed}} = m_{\text{Chamber,Sample,Gas}} - m_{\text{Chamber,Gas}} - \left( m_{\text{Chamber,Sample}} - m_{\text{Chamber}} \right) \left( 1 - \frac{\rho_{\text{BulkGas}}}{\rho_{\text{Skeletal}}} \right) + V_{\text{AdsorbedFilm}} \rho_{\text{BulkGas}} \]

\[ m_{\text{stored}} = m_{\text{Chamber,Sample,Gas}} - m_{\text{Chamber,Gas}} - \left( m_{\text{Chamber,Sample}} - m_{\text{Chamber}} \right) \left( 1 - \frac{\rho_{\text{BulkGas}}}{\rho_{\text{Piece}}} \right) \]

\[ m_{\text{excess adsorbed}} = m_{\text{Chamber,Sample,Gas}} - m_{\text{Chamber,Gas}} - \left( m_{\text{Chamber,Sample}} - m_{\text{Chamber}} \right) \left( 1 - \frac{\rho_{\text{BulkGas}}}{\rho_{\text{Skeletal}}} \right) \]
Methane Uptake measured gravimetrically on powder samples, monoliths measured volumetrically as well.

Values below reported as amount of methane stored using a “powder density” of 0.5 g/ml.

<table>
<thead>
<tr>
<th>ALL-CRAFT Best Performance S-33/k</th>
<th>ANG DOE Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>M/M</td>
<td>N/A</td>
</tr>
<tr>
<td>M/V</td>
<td>118 g/L</td>
</tr>
<tr>
<td>V/V</td>
<td>180 L/L</td>
</tr>
</tbody>
</table>
Small Angle X-ray Scattering

Scattering from a cylinder, with finite thickness.

\[ I(q) = \rho_o^2 \pi r^2 L \]

Scattering in the limit \( L \gg r \)

\[ I(q) \approx 2 \pi \frac{L}{qL} \]

\[ I(q) \approx \frac{2\pi}{L} \]

\[ D_{\text{Surface}} \approx 2.3 \]

\[ I(q) \propto q^{D-6} \]

\[ I(q) = \text{const.} \frac{1}{qL} \left[ \int_0^{qL} \frac{\sin(u)}{u} du - \frac{1 - \cos(qL)}{qL} \right] \]

\[ I(q) \propto \frac{1}{qL} \]

\[ I(q) \propto \frac{1}{qL} \]

Scattered Wave Vector [1/Å]
Computer Modeling of Pore Formation

- Two stage probabilistic cellular automata (PCA) rule (two separate PCA’s in succession).
  - Pore space opened from inside → out
  - Pore space opened from outside → in, creating a spanning cluster
- This models a two stage activation process.
- Qualitatively this model fits well with observed data.
Due to the small size of the pores, ultra high resolution mode was used on the Hitachi S-4700 FESEM. Beam energy was set to 5 kV with a small working distance (3-4mm).

- The beam energy was set to 100 and 120 kV for the JEOL 1200EX TEM.
- Top image SEM on sample S-33/k, showing entrance to pore network.
- Bottom image TEM on sample S-56 showing ~1.5 nm wide pore.
Nitrogen Adsorption Isotherms

- Nitrogen isotherms show evidence of strong microporosity
  - Plateau on linear isotherm
- BET surface area of ~2,200 m²/g for sample S-33/k
- Surface area of most recent samples found to be ~3,000-3,500 m²/g
- Gives total pore volume of 1.22 cc/g, porosity of 0.71
- Note: Surface area for graphene sheet (both sides) is 2,965 m²/g (Chae et. al. Nature Vol 427 2004)
Pore Size Distribution from Nitrogen Isotherm

- Done using non-local density functional theory (NLDFT) assuming slit-shaped pores
- Shows dominance of nanopores, especially pores width ~1.1nm
Methane Adsorption Isotherms

- Langmuir gives good fit of data which is consistent with the hypothesis that surface is covered primarily with a single monolayer of methane.
- Langmuir parameter of $b = 0.814 \text{ MPa}^{-1}$
- Asymptotic value of 288.5 grams of adsorbed methane per kilogram carbon.
- Langmuir fit gives a binding energy of $\sim 22.7 \text{ kJ/mol}$, which is consistent with the high uptake values.
Pore Size Distribution from Methane Isotherm

- Shows dominance of nanopores, especially in pores of width 6-15 Å
- Gives total pore volume of 1.513 cc/g, porosity of 0.752
- Determined via method from Sosin and Quinn, Carbon 34 1335 (1996)
## Comparison of Methods

<table>
<thead>
<tr>
<th></th>
<th>Porosity</th>
<th>Total Pore Volume [cc/g]</th>
<th>Micropore (pore diameter 0.5–2 nm) Volume [cc/g]</th>
<th>Mesopore (2–50 nm) Volume [cc/g]</th>
<th>Macropore (&gt;50 nm) Volume [cc/g]</th>
<th>Average Nanopore Width [Å]</th>
<th>Average Nanopore Length [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.752</td>
<td>1.513</td>
<td>1.197</td>
<td>0.254</td>
<td>0.062</td>
<td>~11</td>
<td>N/A</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.710</td>
<td>1.222</td>
<td>1.107</td>
<td>0.094</td>
<td>0.021</td>
<td>~11</td>
<td>N/A</td>
</tr>
<tr>
<td>SAXS</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>~4</td>
<td>~15</td>
</tr>
</tbody>
</table>

**Graph**

- **X-axis**: Pore Width Range [nm]
- **Y-axis**: Pore Volume [cc/g]
- **Legend**: Methane (blue), Nitrogen (red)

**TEM Image**

- Scale: 10 nm
Activated Carbon made from Missouri corn cob has proven to be an excellent candidate for alternative fuel storage at a low cost.

Department of energy target of 118 g/L has been met.

Carbon has been analyzed with a variety of methods which give consistent results.

Carbon is still being optimized.

Still getting results from the test fixture on the pickup.

Shows promise for hydrogen storage as well (Mikael Wood et. al. 1:51 PM today in room 502).
Non-Local Density Functional Theory (NLDFT) for slit-shaped pores was used. The relationship between this theory and the experimental data is given by the generalized adsorption isotherm (GAI)

\[ N\left(\frac{P}{P_0}\right) = \int_{W_{\text{MIN}}}^{W_{\text{MAX}}} N\left(\frac{P}{P_0},W\right)f(W)\,dW \]

where \( N(P/P_0) \) is the experimental adsorption isotherm data, \( W \) is the pore width, \( N(P/P_0,W) \) is the isotherm on a single pore of width \( W \), and \( f(W) \) is the pore size distribution function.
Brunauer-Emmett-Teller Surface Area

- Most widely used method for determination of surface area of solids
- BET Formula given by:

\[
\frac{m}{m_{\text{mono}}} = \frac{CP}{P_0} \left(1 - \frac{P}{P_0}\right) \left(1 + (C - 1)\frac{P}{P_0}\right)
\]

- where \( m \) is the mass of gas adsorbed at a relative pressure \( (P/P_0) \) (\( P_0 \) taken as the saturation pressure of adsorptive gas), \( m_{\text{mono}} \) is the mass of adsorbate constituting a monolayer of surface coverage, and \( C \) is the BET constant.
BET Theory Cont.

- BET equation in linear form:

\[
\frac{P}{P_0} = \frac{1}{C m_{\text{mono}}} + \frac{C - 1}{C m_{\text{mono}}} \frac{P}{P_0} \]

\[
\text{intercept} = \frac{1}{C m_{\text{mono}}} \]

\[
\text{slope} = \frac{C - 1}{C m_{\text{mono}}} \]

\[
\therefore m_{\text{mono}} = \frac{1}{\text{slope} + \text{intercept}}
\]

- Total Surface Area:

\[
S_{\text{Total}} = \frac{m_{\text{mono}} N A A_{\text{CrossSection}}}{M}
\]

- \(N_A\) is Avogadro’s number, \(A_{\text{CrossSection}}\) is the cross-sectional area of the gas molecule, and \(M\) is the molecular mass of the gas.

- \(A_{\text{CrossSection}}\) for Nitrogen is 16.2 Å²/molecule
Methane Binding Energy

\[ b(T) = \text{Langmuir parameter} = \frac{1}{p_0 \sqrt{T}} \left( \frac{q}{RT} \right) \]

\[ p_0, T_0 \text{ are the reference pressure and temperature} \]
\[ T \text{ is the Absolute temperature = room temperature (293 K)} \]
\[ R \text{ is the Specific Gas Constant = } \frac{\text{Universal Gas Constant}}{\text{Molar Mass}} \]
\[ R \approx 0.52 \frac{J}{g \cdot K} \text{ for methane} \]

\[ q = \text{specific heat of adsorption} = RT \ln \left( b p_0 \sqrt{\frac{T}{T_0}} \right) \]

\[ q = 152.4 \frac{J}{g} \ln \left( 0.814 \text{ MPa}^{-1} p_0 \sqrt{\frac{293 \text{ K}}{T_0}} \right) \]
Methane Binding Energy

Localized Adsorption

\[ b = e^{-U_{00}/(kT)} \frac{1}{\nu_x \nu_y \nu_z} \sqrt{\frac{kT}{8\pi^3 m^3}} \]

\[ U_0(x, y) \equiv \min_{0<z<\infty} U(x, y, z) \]

\[ \varepsilon \equiv - \left[ U_{00} + \frac{1}{2} h(\nu_x + \nu_y + \nu_z) \right] \]

\[ \text{assume } \nu_x = \nu_y = \nu_z \]

\[ b = 0.814 \text{ MPa}^{-1} \]

\[ \nu_z = 3.00 \times 10^{12} \text{ s}^{-1} \]

\[ m = (0.0160 \text{ kg/mol}) / N_A \]

\[ T = 293 \text{ K} \]

\[ N_A \varepsilon = 22.7 \text{ kJ/mol} \]


Why are Nanopores Important?

\[3.7 \text{ Å} \sim 11 \text{ Å} \]

\[1.9 \text{ Å} \sim 4 \text{ Å} \]

\[\sim 224 \text{ Å} \]
Small Angle X-ray Scattering

Scattering in the limit L >> r

\[ I(q) = \rho_o^2 \pi r^2 L \]

Scattering from a cylinder, with finite thickness.

\[ I(q) = \text{const.} \frac{1}{qL} \left[ \frac{qL}{u} \int_0^{\frac{qL}{u}} \sin(u) \, du - \frac{1 - \cos(qL)}{qL} \right] \]

\[ I(q) \propto \frac{2\pi}{L} \]

\[ I(q) \propto \frac{1}{qL} \]

Scattering in the limit L >> r

\[ D_{\text{Surface}} \approx 2.3 \]