Developing a Novel Ultrafine Coal Dewatering Process (04-VaT-P1-32: Coal Beneficiation)

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Outline

- Background and motivation
- Project goal, proposed approach, and advantages
- Methods
- Results
  - Solvent recovery by filtration
  - Solvent recovery by drying
- Conclusions
Dewatering fine coal is important for both coal beneficiation and the environment

- 70-90 million tons of fine coal tailings discarded each year in the US

- Dewatering by mechanical means has reached its limit

- Dewatering by thermal drying is energy-intensive
  - One of the most energy-intensive processes in industry due to the high enthalpy cost of phase change (Mujumdar and Wu, 2007)
Hydrophobic-Hydrophilic Separation (HHS)

- **Step I**: Wet Coal
- **Step II**: Dry Coal

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Boiling Point $^1$ (°C)</th>
<th>Heat of Vaporization $^2$ kJ/mole</th>
<th>kJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (H$_2$O)</td>
<td>100.0</td>
<td>40.7</td>
<td>2,257</td>
</tr>
<tr>
<td>Butane (C$<em>4$H$</em>{10}$)</td>
<td>-0.5</td>
<td>22.4</td>
<td>386</td>
</tr>
<tr>
<td>Pentane (C$<em>5$H$</em>{12}$)</td>
<td>36.1</td>
<td>25.8</td>
<td>358</td>
</tr>
<tr>
<td>Hexane (C$<em>6$H$</em>{14}$)</td>
<td>68.7</td>
<td>28.9</td>
<td>336</td>
</tr>
<tr>
<td>Heptane (C$<em>7$H$</em>{16}$)</td>
<td>98.4</td>
<td>31.7</td>
<td>317</td>
</tr>
</tbody>
</table>

$^1$ Boiling Point
$^2$ Heat of Vaporization
Results Obtained with a Sub-bituminous Coal

<table>
<thead>
<tr>
<th>Particle Size (mm)</th>
<th>Moisture (%wt)</th>
<th>Ash (%wt)</th>
<th>Heat Value (Btu/lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.350</td>
<td>3.20</td>
<td>9.92</td>
<td>10,827</td>
</tr>
<tr>
<td>0.600</td>
<td>3.20</td>
<td>9.82</td>
<td>11,019</td>
</tr>
<tr>
<td>1.180</td>
<td>2.87</td>
<td>8.4</td>
<td>11,216</td>
</tr>
<tr>
<td>6.300</td>
<td>2.30</td>
<td>6.27</td>
<td>11,529</td>
</tr>
</tbody>
</table>

Solvent recovery is essential for the economic operation of HHS

- Low solvent loss (<~1400 ppm solvent in coal product or 0.56 gallon/ton coal)
- Low equipment/capital cost
- Low operation cost
Goal: to develop an efficient solvent recovery system for the HHS process

Approach – in-situ recovery combining filtration and drying
- recover the bulk of solvents by pressure filtration
- recover the small amount of residual solvents by in-situ evaporation

Key advantages
- Only a small fraction of solvents is removed through phase change → energy efficient
- A single device is used in separation and drying → low equipment cost
Solvent vaporization and removal by a carrier gas

Underlying physics
- Thermal transport
- Liquid solvent evaporation
- Transport of multi-component gas mixtures

Pore-scale model
Gas transport model

Dusty gas model: \[ \sum_{j=1}^{n} \frac{x_j J_i - x_i J_j}{\rho_i D_{ij}} + \frac{J_i}{\rho_i D_{ik}} = -\frac{1}{p} \frac{dp_i}{dz} - \frac{x_i k_p}{\mu D_{ik}} \frac{dp}{dz} \quad (i = 1, 2, \ldots n) \]

\[ J_1 = \rho_1 u_1 = -\left( \left( \frac{x_1 D_{2k} D_{1k} + D_{12} D_{1k}}{x_2 D_{1k} + x_1 D_{2k} + D_{12}} + \frac{k_p \rho_1 R g T}{\mu} \right) \frac{d\rho_1}{dz} + \left( \frac{x_1 D_{2k} D_{1k}}{x_2 D_{1k} + x_1 D_{2k} + D_{12}} + \frac{k_p \rho_1 R g T}{\mu} \right) \frac{d\rho_2}{dz} \right) \]

\[ J_2 = \rho_2 u_2 = -\left( \left( \frac{x_2 D_{2k} D_{1k}}{x_2 D_{1k} + x_1 D_{2k} + D_{12}} + \frac{k_p \rho_2 R g T}{\mu} \right) \frac{d\rho_1}{dz} + \left( \frac{x_2 D_{2k} D_{1k} + D_{12} D_{2k}}{x_2 D_{1k} + x_1 D_{2k} + D_{12}} + \frac{k_p \rho_2 R g T}{\mu} \right) \frac{d\rho_2}{dz} \right) \]

Effective permeability (with slippage effect): \[ k_p = \frac{r_0^2}{8} \left( 1 + 4 Kn \left( \frac{2}{\sigma_v} - 1 \right) \right) \]

Knudsen diffusion: \[ D_{ik} = \frac{2r_0}{3} \frac{\sqrt{8 k_B T}}{\pi m_i} \quad (i = 1, 2) \]

Mutual diffusion: \[ D_{12} = \left( D_{x_1 \rightarrow 1} \right)^{x_1} \left( D_{x_1 \rightarrow 0} \right)^{1-x_1} \]

\[ D_{x_i \rightarrow 1} = \frac{2}{3} \frac{\sqrt{m_i k_B T / \pi}}{M_i \sigma_i \rho_i} \quad (i = 1, 2) \]

Viscosity for mixture gas: \[ \mu = \frac{\mu_1}{1 + \frac{x_2 1.385 \mu_1}{x_1 D_{12} \rho_1}} + \frac{\mu_2}{1 + \frac{x_1 1.385 \mu_2}{x_2 D_{12} \rho_2}} \]
Evaporation and radial mass transfer

- Limit of evaporation Kinetics (evaporation << diffusion):
  
  Schrage equation
  \[ \dot{m}_k = \frac{2\sigma}{2-\delta} \left( \frac{M_2}{2\pi R_g} \right)^{0.5} \left( \frac{p_{sat}}{\sqrt{T_i}} - \frac{p_2}{\sqrt{T_v}} \right) \]

- Limit of vapor transport (evaporation >> diffusion):
  
  Vapor diffusion
  \[ \dot{m}_t \sim D_s M_2 (\rho_{sat} - \rho_2)/r_0 \]

- Ratio:
  \[ \frac{\dot{m}_k}{\dot{m}_t} \sim \frac{2r_0}{D_s} \left( \frac{R g T}{2\pi M_2} \right)^{0.5} = 7.5 \gg 1 \]

  Vapor diffusion is more rate-limiting than evaporation kinetics

Quasi-static condition at any cross section

\[ \dot{m}_{evp} = \alpha (\rho_{sat} - \rho_2) \quad \alpha = Sh \times D_s / 2r_0 \]
Conservation laws

\[ \frac{\partial \rho_1}{\partial t} = - \frac{\partial J_1}{\partial z} \]
\[ \frac{\partial \rho_2}{\partial t} = - \frac{\partial J_2}{\partial z} + 2\dot{m}_{evp}/r_0 \]
\[ \rho_{liq} \frac{\partial h}{\partial t} = -\dot{m}_{evp} \]

Initial and boundary conditions

Initial conditions
\[ \rho_1(t = 0) = \frac{p_d}{R_g T} - \rho_{sat} \]
\[ \rho_2(t = 0) = \rho_{sat} \]
\[ h(t = 0) = h_0 \]

boundary conditions
\[ z = 0: \rho_1 + \rho_2 = \frac{p_u}{R_g T} \]
\[ z = 0^-: J_2 = 0 \]
\[ z = L: \rho_1 + \rho_2 = \frac{p_d}{R_g T} \]
\[ z = L: \frac{\partial \rho_2}{\partial z} = 0 \]
Stage 1: pressure filtration to remove bulk of solvents

- Pressurized room-temperature N$_2$ as the agent
- Solvent-coal slurries are pressure filtered
Stage 2: solvent vaporization and removal

- Evaporation and mass convection

- Operating temperature must be elevated for some solvents

- Room-temperature $N_2$, heated $N_2$, and superheated steam as carrier gas
Stage 2: solvent vaporization and removal
Stage 2: solvent vaporization and removal

Method – Solvent Vaporization and Removal
Stage 2: solvent vaporization and removal

Device fabrication, shake-down, and tuning accomplished in 11/2020

Michael Huylo
Coal: Met Warrior Clean Coal

Solvents: pentane and hexane

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Viscosity (mPa·s)</th>
<th>Boiling point (°C)</th>
<th>Vapor pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>0.250</td>
<td>36.0</td>
<td>57.3</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.310</td>
<td>69.0</td>
<td>16.0</td>
</tr>
</tbody>
</table>

$D_{50} = 13.1 \, \mu\text{m}$; $D_{80} = 43.3 \, \mu\text{m}$
Stage 1: pressure filtration for bulk solvent removal

- Nonlinear filtration kinetics due to cake formation and three phase flow in cakes
- Gas breakthrough occurs within 60 s even at the lowest pressure difference → compatible with HHS technologies
Stage 1: pressure filtration for bulk solvent removal

- filtration curves for 10-15% hexane-coal slurries at various pressure differences
- Slurries with 10% mass loading are selected in subsequent studies
- Solvent: pentane and hexane
Results – Filtration Cake Properties

- Analytical model for pressure filtration

\[ \frac{dV}{dt} = \frac{A^2 \Delta P}{\mu \left( \frac{8X_s V}{kR^2 \rho_s} \frac{1}{1 - k} \frac{1}{1 + b/4R} + AR_m^r \right)} \]

Huang, Pan, and Yoon, *Minerals Eng.*, 115, 88, 2018
Drying using room-temperature N₂

- Pentane and hexane are removed to acceptable concentration (1400ppm) in 105 and 230 s
- Drying rate decreases during the late stage of solvent removal
- Drying time is far longer than desired (within 10 s for integration with HHS)
Drying of pentane-loaded cakes by room-temperature $N_2$

- Cake properties taken from measurement and filtration model fitting
- Dropping drying rate accommodated by dividing residual solvents in filtration cakes into two populations
- Model revealed that gas at cake exit is not saturated with solvent vapor
Results – Drying by Heated $\text{N}_2$

- Drying of solvent-loaded filtration cakes by heated $\text{N}_2$

- Heating $\text{N}_2$ to 100°C and 150°C reduces drying time, but not significant enough
- Increasing pressure difference reduces drying time, but still not enough
- Transport of vapor from solvent evaporation site to carrier gas streams in filtration cake limits the drying rate
Drying of solvent-loaded filtration cakes by superheated steam

- Superheated steam greatly accelerates drying
- Increasing pressure greatly accelerates drying
- Superfast heating (and possibly perturbation of cake structure by water condensation and evaporation) responsible for fast drying
- Final water content in coal cake <5% \(\rightarrow\) acceptable for commercial coal handling
Drying of filtration cakes formed by Vacuum filtration

- Vacuum filtration is sometimes preferred over pressure filtration due to lower equipment cost.
- Vacuum-formed filtration cake is less compact.

Sub-10s drying time achieved!
Summary

- **An *in-situ* solvent recovery method** for recovering solvents from solvent-ultrafine coal slurries is proposed.
- **Bench-scale tests confirmed** the effectiveness of the proposed method:
  - Pressure filtration can be accomplished in less than 60 s at realistic coal loading (10-15%).
  - Using superheated steam as carrier gas, the solvents in the final filtration cake can be reduced below 1400 ppm in less than 10 s.
- **The project cleared the way** for pilot-scale development of the proposed method.

Fruitful collaboration with Dr. Evan Granite of NETL is gratefully acknowledged.