Carbon Dioxide (CO₂) Uses

Emerging Industrial Uses of CO₂

- Enhanced Coal Bed Methane Recovery
- Algal bio-fixation and bio-fuel production
- Enhanced Geothermal Systems (using CO₂ as a working fluid)
- Bauxite residue processing
- Power Generation with CO₂ as a working fluid
- Carbonate mineralisation (aggregate production)
- Polymer Processing
- CO₂ concrete curing

Reference: at end of presentation
Carbon Dioxide ($\text{CO}_2$) Uses cont.

Existing Industrial Uses of $\text{CO}_2$

- Winemaking
- Steel Manufacture
- Pulp and Paper processing
- Metal Working
- Water Treatment
- Electronics
- Inerting
- Pneumatics

Reference: at end of presentation
Carbon Dioxide (CO₂) Uses cont.

Existing Industrial Uses of CO₂

- Enhanced Oil Recovery
  - 50Mtpa
  - Other Oil and Gas applications

- Urea fertiliser production
  - 'Captive' use

- Food processing, preservation and packaging

- Beverage Carbonation

- Coffee Decaffeination

- Pharmaceuticals

- Horticulture

- Fire suppression

Reference: at end of presentation
Outline

- Supercritical Fluids
- Decaffeination
- Beverage Carbonation
- Cryogenic Freezing
- Water Treatment
Supercritical Fluids

Phase Diagram of Carbon Dioxide

Supercriticality

At the initial condition the liquid and vapor phase coexist.

Heating

- Initial condition
  - $T_i = 28^\circ C$
  - $P_i = 69$ bar

- Density arrangement:
  - Green floater
  - Supercritical phase
  - Red floater

- Density supercritical phase
  - $\rho = 468$ kg/m$^3$

- Density vapor phase
  - $\rho = 320$ kg/m$^3$
  - $\rho = 600$ kg/m$^3$

...therefore, the lighter green floater swims on the supercritical phase, while the heavier red floater sinks to the bottom.
### CO₂ vs. Other Supercritical Fluids

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Critical Temperature (°C)</th>
<th>Critical Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide</td>
<td>31.1</td>
<td>73.8</td>
</tr>
<tr>
<td>Chlorotrifluoromethane</td>
<td>28.9</td>
<td>39.2</td>
</tr>
<tr>
<td>Propane</td>
<td>96.7</td>
<td>42.5</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>280.3</td>
<td>40.7</td>
</tr>
<tr>
<td>Toluene</td>
<td>318.6</td>
<td>41.1</td>
</tr>
<tr>
<td>Perchloroethylene</td>
<td>347</td>
<td>47.6</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>237</td>
<td>61</td>
</tr>
<tr>
<td>Water</td>
<td>374.2</td>
<td>220.5</td>
</tr>
</tbody>
</table>

- Dry Cleaning
- Spray Paint
- Coffee Decaffeination
- Perchloroethylene
- Chlorofluorocarbon or propane
- Water, Methylene Chloride

Reference: at end of presentation
Choose CO$_2$ as a SC Fluid

- Safe, environmentally friendly
- Recyclable
- Inexpensive/readily available
- No residue
- Mild conditions for supercriticality
- Tunable
- Servicing the environment by using CO$_2$

Venus’s atmosphere is 96.5% CO$_2$ and the average temperature and pressure are 467°C & 93 bar, meaning the atmosphere on Venus is made up of supercritical CO$_2$!
Market for Coffee

- The coffee industry is valued at $100 billion annually; $19 billion just in the US
  - Largest worldwide commodity after crude oil
- Worldwide, we drink 500 billion cups of coffee per year
- Decaffeinated coffee accounts for about 12% of worldwide consumption
- Certified coffee farms dropped from 43% to 24% between 1996 and 2010 because of demand
- There are about 1,200 chemical compounds in coffee with about half contributing to flavor
Coffee Decaffeination

- Caffeine is a nonpolar, hydrophilic molecule
- Water as a solvent
- Organics as solvents
- Supercritical CO₂ is tunable
  - Selectively dissolve caffeine
  - Increasing pressure increases the density and makes the supercritical CO₂ simulate greater polarity
Water as a Solvent—Swiss Water Process

- Uses clean water
- Wastes a set of coffee beans

Reference: at end of presentation

Fig. 1. Conventional ‘water process’ for decaffeination of coffee beans.
Beans amount to 95% of cost

- Water waste is a major source of “anti-greenness”

**Table 2.1 Physical input/output table for 1 ton of green bean input (simplified)**

<table>
<thead>
<tr>
<th>Input</th>
<th>Physical amount</th>
<th>Output</th>
<th>Physical amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green beans</td>
<td>1,000 kg</td>
<td>Green beans grade A</td>
<td>430 kg</td>
</tr>
<tr>
<td>Water</td>
<td>0.035 m³</td>
<td>Green beans grade B</td>
<td>370 kg</td>
</tr>
<tr>
<td>Electric energy</td>
<td>40 kWh</td>
<td>Green beans grade C</td>
<td>60 kg</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Green beans grade D</td>
<td>55 kg</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Green beans for local</td>
<td>75 kg</td>
</tr>
<tr>
<td></td>
<td></td>
<td>market</td>
<td></td>
</tr>
<tr>
<td>Dust</td>
<td>2 kg</td>
<td>Weight loss</td>
<td>8 kg</td>
</tr>
<tr>
<td>Waste water</td>
<td>0.035 m³</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reference: at end of presentation
Supercritical CO$_2$ Decaffeination

Without the use of water, extraction will result in solid caffeine byproduct when CO$_2$ is depressurized into a gas.

Fig. 2. Decaffeination of coffee beans using supercritical CO$_2$. MeCl$_2$ refers to methylene chloride.

Reference: at end of presentation
Market for Beverage Carbonation

- Dominant use of CO₂ in the food industry
- Solution of carbon dioxide gas in liquid water

- Why?
- Creates “bubbly effect”
- Acts as a preservative

Reference: at end of presentation
Carbonation Process

- Carbonator or Saturator used to carbonate water
- Carbonated water mixed with syrups and additives

Reference: at end of presentation
Cryogenic Freezing

- Defined as freezing at -75°F or below.
- CO₂ injected as high pressure liquid
- Instantly expands into gas and tiny solid particles called “snow”
- Solids are driven into surface of the food
- The refrigeration effect occurs due to the latent heat of sublimation

Reference: at end of presentation
## Cryogenic Freezing vs. Mechanical Freezing

<table>
<thead>
<tr>
<th></th>
<th>Cryogenic Freezing</th>
<th>Mechanical Freezing</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Investment Costs</strong></td>
<td>Lower cost of capital equipment and simpler, inexpensive installation.</td>
<td>Higher cost of capital equipment and complex and costly installation.</td>
</tr>
<tr>
<td><strong>Operating Costs</strong></td>
<td>Higher energy cost with liquid nitrogen or carbon dioxide as energy source.</td>
<td>Generally lower energy cost</td>
</tr>
<tr>
<td><strong>Maintenance Costs</strong></td>
<td>Low:</td>
<td>High:</td>
</tr>
<tr>
<td></td>
<td>• High uptime</td>
<td>• All parts of a mechanical refrigeration system consisting of three major pieces: high horse-power compressor, condenser, evaporator, and refrigerant storage must be inspected annually.</td>
</tr>
<tr>
<td></td>
<td>• Low maintenance requirements</td>
<td>• Ammonia refrigeration systems with 10,000 pounds or more of ammonia are a covered process subject to the requirements of the OSHA Process Safety Management Standard (PSM) 1910.119.</td>
</tr>
<tr>
<td></td>
<td>• Reduced cleaning requirements</td>
<td></td>
</tr>
<tr>
<td><strong>Freezing Temperatures</strong></td>
<td>Typically, -160°F or lower for Liquid N₂ and -80°F for liquid CO₂.</td>
<td>Typically -30°F</td>
</tr>
<tr>
<td><strong>Food Quality</strong></td>
<td>Rapid freezing reduces dehydration loss to less than 1%, thus preserving texture and flavor.</td>
<td>Slower freezing, up to 3 to 4 times longer than cryogenic freezing, can result in surface dehydration and weight loss and does not allow the successful preparation of Individually Quick Frozen (IQF) products.</td>
</tr>
<tr>
<td></td>
<td>Product does not stick to belt</td>
<td>Product tends to stick to belt</td>
</tr>
<tr>
<td><strong>Environmental Considerations</strong></td>
<td>Environmentally friendly way of freezing food.</td>
<td>Ammonia is a great refrigerant but it is highly toxic.</td>
</tr>
</tbody>
</table>

Reference: at end of presentation
CO₂ Water Treatment: pH Control

- CO₂ is inert & non-corrosive
- Gradual pH level changes vs. rapid strong acid changes
- Secondary products are safe for the environment vs. mineral acids

Reference: at end of presentation
Summary

• Abundant source of CO₂ in atmosphere
• Various uses for CO₂
• All greener methods than current methods
  • Readily available
  • No hazardous byproducts during usage
  • Can be used with existing systems and materials
References

Supercritical Fluids & Decaffeination

- “Pure Component Properties” (queriable database). Chemical Engineering Research Information Center.

Cryogenic Freezing & Carbonation

References (cont.)

References (cont.)

Water Treatment & CO2 Usage Summary
- Brinckerhoff, P. Accelerating the Uptake of CCS: Industrial Use Capture of Carbon Dioxide
- Sciencedirect.com,. Carbon capture, storage and utilisation technologies: A critical analysis and
  comparison of their life cycle environmental impacts
- Theenergycollective.com,. Carbon Dioxide and Recycling Use | The Energy Collective
  (accessed May 1, 2015).
  (accessed May 1, 2015).