Managing Emissions from Fossil Resources

A Challenge to Technology and Policy

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IPCC Model Simulations of CO$_2$ Emissions

![Graph showing IPCC model simulations of CO$_2$ emissions.](image)
Growth in Emissions

Year
2000 2010 2020 2030 2040 2050 2060 2070 2080 2090 2100
Fractional Change
0 2 4 6 8 10 12 14 16 18

- Constant Growth 1.6%
- Plus Population Growth to 10 billion
- Closing the Gap at 2%
- Energy intensity drop 1% per year
- Energy intensity drop 1.5% per year
- Energy intensity drop 2% per year

SUSTAINABLE ENERGY
Table 9  Aggregation of global fossil energy sources—all occurrences, in Gtoe

<table>
<thead>
<tr>
<th></th>
<th>Consumption 1860–1994</th>
<th>1994</th>
<th>Reserves</th>
<th>Resources</th>
<th>Resource base</th>
<th>Additional occurrences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conventional</td>
<td>103</td>
<td>3.21</td>
<td>150</td>
<td>145</td>
<td>295</td>
<td></td>
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<tr>
<td>Unconventional</td>
<td>6</td>
<td>0.16</td>
<td>183</td>
<td>336</td>
<td>519</td>
<td>1,824</td>
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<tr>
<td>Natural gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Conventional</td>
<td>48</td>
<td>1.87</td>
<td>141</td>
<td>279</td>
<td>420</td>
<td></td>
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<tr>
<td>Unconventional</td>
<td>—</td>
<td>—</td>
<td>192</td>
<td>258</td>
<td>450</td>
<td>387</td>
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<tr>
<td>Clathrates</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>18,759</td>
</tr>
<tr>
<td>Coal</td>
<td>134</td>
<td>2.16</td>
<td>1,003</td>
<td>2,397</td>
<td>3,400</td>
<td>2,846</td>
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<tr>
<td>Total fossil occurrences</td>
<td>291</td>
<td>7.40</td>
<td>1,669</td>
<td>3,415</td>
<td>5,084</td>
<td>23,815</td>
</tr>
</tbody>
</table>

H.H. Rogner, 1997

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aSources: Historical consumption (46). Reserves, resources, and occurrences, see Tables 2–8.

— = negligible volumes.

bReserves to be discovered or resources developed to resources.

cResource base is the sum of reserves and resources.

dIncludes natural gas liquids.
Carbon as a Low-Cost Source of Energy

Cumulative Carbon Consumption as of 1997

US1990$ per barrel of oil equivalent

Lifting Cost

Cumulative Gt of Carbon Consumed

H.H. Rogner, 1997
Fossil fuels are fungible
The Challenge: Holding the Stock of CO₂ constant

- Constant emissions at 2010 rate
- 33% of 2010 rate
- 10% of 2010 rate
- 0% of 2010 rate
Orders of Magnitude
A Triad of Large Scale Options

• Solar
  – Cost reduction and mass-manufacture

• Nuclear
  – Cost, waste, safety and security

• Fossil Energy
  – Zero emission, carbon storage and interconvertibility

Markets will drive efficiency, conservation and alternative energy
Small Energy Resources

- Hydro-electricity
  - Cheap but limited
- Biomass
  - Sun and land limited, severe competition with food
- Wind
  - Stopping the air over Colorado every day?
- Geothermal
  - Geographically limited
- Tides, Waves & Ocean Currents
  - Less than human energy generation
CCS is technically feasible

It is affordable

It can start today

It is likely to be a major contributor to CO₂ reductions worldwide
Dividing The Fossil Carbon Pie

900 Gt C total

Past

10yr

550 ppm
Removing the Carbon Constraint

5000 Gt C
total
Net Zero Carbon Economy

CO₂ from concentrated sources
- Capture from power plants, cement, steel, refineries, etc.

CO₂ from distributed emissions
- Capture from air

Permanent & safe disposal
- Geological Storage
- Mineral carbonate disposal
**Net Zero Carbon Economy**

- **CO₂ from concentrated sources**
  - Capture from power plants, cement, steel, refineries, etc.

- **CO₂ from distributed emissions**
  - Capture from air

- Permanent & safe disposal
  - Geological Storage
    - Mineral carbonate disposal

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[Logo: LENFEST CENTER FOR SUSTAINABLE ENERGY]
Underground Injection
Gravitational Trapping
Subocean Floor Disposal

a

Seafloor


Hydrates


CO₂(l)

CO₂(aq)

NBZ

HFZ

b

Seafloor


Hydrates


CO₂(l)

CO₂(aq)

c

Seafloor


CO₂(aq)
Energy States of Carbon

The ground state of carbon is a mineral carbonate.

- **Carbon**
  - Energy: 400 kJ/mole

- **Carbon Dioxide**
  - Energy: 60...180 kJ/mole

- **Carbonate**
Bedrock geology GIS datasets – All U.S. (Surface area)

Legend
- ultramafic rock

Total = 9820 ±100 km²
Mineral Sequestration

\[
\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{CO}_2(\text{g}) \rightarrow 3\text{MgCO}_3 + 2\text{SiO}_2 + 2\text{H}_2\text{O(1)} + 63 \text{kJ/mol CO}_2
\]
Belvidere Mountain, Vermont
Serpentine Tailings
Oman Peridotite

Photo: Juerg Matter
Net Zero Carbon Economy

CO₂ from concentrated sources
Capture from power plants, cement, steel, refineries, etc.

CO₂ from distributed emissions
Capture from air

Permanent & safe disposal
Geological Storage
Mineral carbonate disposal
Many Different Options

- Flue gas scrubbing
  - MEA, chilled ammonia
- Oxyfuel Combustion
  - Naturally zero emission
- Integrated Gasification Combined Cycle
  - Difficult as zero emission
- AZEP Cycles
  - Mixed Oxide Membranes
- Fuel Cell Cycles
  - Solid Oxide Membranes
Zero Emission Principle

$CO_2$, $N_2$, $H_2O$, $SO_x$, $NO_x$ and other Pollutants
Boudouard Reaction

Decarbonizer

Gasifier Reducer

Fuel Cell Oxidizer

$\text{CO}_2 \rightarrow 2\text{CO}$

$2\text{CO} \rightarrow 2\text{CO}_2$
Carbon makes a better fuel cell

\[ \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \]
- no change in mole volume
- entropy stays constant
- \( \Delta G = \Delta H \)

\[ 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \]
- large reduction in mole volume
- entropy decreases in reactants
- made up by heat transfer to surroundings
- \( \Delta G < \Delta H \)
Proposed Membrane

Phase I: Solid Oxide

Phase II: Molten Carbonate

Multi-Phase Equilibrium

\[ \text{CO}_2 + \text{O}^{2-} = \text{CO}_3^{2-} \]
Net Zero Carbon Economy

CO₂ from concentrated sources

CO₂ extraction from air

Permanent & safe disposal
Air Capture: A Different Paradigm

• Leave existing infrastructure intact
• Retain quality transportation fuels
• Eliminate shipping of CO₂
• Open remote sites for CO₂ disposal
• Enable fuel recycling with low cost electricity

Separate Sources from Sinks
Relative size of a tank

- **gasoline**
- **hydrogen**

Electrical, mechanical storage

Batteries etc.
Challenge: CO$_2$ in air is dilute

• Energetics limits options
  – Work done on air must be small
    • compared to heat content of carbon
    • 10,000 J/m$^3$ of air
• No heating, no compression, no cooling
• Low velocity 10m/s (60 J/m$^3$)

Solution: Sorbents remove CO$_2$ from air flow
CO₂ Capture from Air

1 m³ of Air
40 moles of gas, 1.16 kg
wind speed 6 m/s

\[
\frac{mv^2}{2} = 20 \text{ J}
\]

0.015 moles of CO₂
produced by 10,000 J of gasoline
Ca(OH)₂ as an absorbent

CO₂ mass transfer is limited by diffusion in air boundary layer
How much wind? (6 m/sec)

Wind area that carries 10 kW

0.2 m² for CO₂

Wind area that carries 22 tons of CO₂ per year

50 cents/ton of CO₂ for contacting

80 m² for Wind Energy
A First Attempt

Air contactor:
\[ 2\text{Na(OH)} + \text{CO}_2 \rightarrow \text{Na}_2 \text{CO}_3 \]

Ion exchanger:
\[ \text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow 2\text{Na(OH)} + \text{CaCO}_3 \]

Calciner:
\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]
(1) $2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ \quad \Delta H^0 = -171.8 \text{ kJ/mol}$

(2) $\text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow 2\text{NaOH} + \text{CaCO}_3$ \quad \Delta H^0 = 57.1 \text{ kJ/mol}$

(3) $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ \quad \Delta H^0 = 179.2 \text{ kJ/mol}$

(4) $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$ \quad \Delta H^0 = -64.5 \text{ kJ/mol}$

(5) $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ \quad \Delta H^0 = -890.5 \text{ kJ/mol}$

(6) $\text{H}_2\text{O} \ (l) \rightarrow \text{H}_2\text{O} \ (g)$ \quad \Delta H^0 = 41. \text{ kJ/mol}$
Cost of Contacting the Air

Unit Cost

\(1/\rho\)
Cost of CO$_2$ from Air
Sorbent Choices

![Graph showing binding energy vs. CO2 partial pressure for different temperatures (300K and 350K) and sources (Air and Power plant).](image)
Cost of CO$_2$ from Air (rescaled)
60m by 50m

3kg of CO$_2$ per second

90,000 tons per year

4,000 people or

15,000 cars

Would feed EOR for 800 barrels a day.

250,000 units for worldwide CO$_2$ emissions
The first of a kind
Materially Closed Energy Cycles

Energy Source → \( H_2 \) → Energy Consumer

\( O_2 \) → \( H_2O \) → \( H_2O \) → \( O_2 \)
Materially Closed Energy Cycles

Energy Source $\rightarrow H_2 \rightarrow CO_2 \rightarrow CH_2 \rightarrow O_2 \rightarrow H_2O \rightarrow H_2O \rightarrow CO_2 \rightarrow O_2$

LENFEST CENTER FOR SUSTAINABLE ENERGY
Fuels

Oxidizer Combustion products

Biomass

CO

Fischer Tropsch Synthesis Gas

Methanol

Ethanol

Natural Gas

Town Gas

Petroleum

Coal

Gasoline

Methane

Benzene

Carbon

Increasing Hydrogen Content

Increasing Oxidation State

Free O₂

Free C-H

Oxygen

CO₂

H₂O

Carbon

Hydrogen

Increasing Hydrogen Content

Combustion products

Fuels

Oxidizer

LENFEST CENTER FOR SUSTAINABLE ENERGY
Fuels Oxidizer Combustion products
Biomass CO Fischer Tropsch Synthesis Gas
Methanol Ethanol Natural Gas
Petroleum Town Gas Gasoline
Coal Free O₂ Free C-H
Increasing Hydrogen Content
Increasing Oxidation State
Oxygen
H₂O
CO₂

Lenfest Center for Sustainable Energy
Fuels

Oxidizer Combustion products

Biomass CO Fischer Tropsch Synthesis Gas Methanol Ethanol Natural Gas Town Gas Petroleum Coal Gasoline Benzene Carbon Hydrogen

Increasing Hydrogen Content
Increasing Oxidation State

Free O₂
Free C-H

Oxygen
CO₂
H₂O

Oxidizer
Combustion products
Fuels

LENFEST CENTER FOR SUSTAINABLE ENERGY
Carbon Capture and Storage
for
Carbon Neutral World

• CCS simplifies Carbon Accounting
  - Ultimate Cap is Zero
  - Finite amount of carbon left
Public Institutions and Government

Carbon Board

Private Sector
- Carbon Extraction
- Farming, Manufacturing, Service, etc.
- Carbon Sequestration

Certified Carbon Accounting

Guidance

Permits & Credits

Certification

Certificates