Sustainability and Carbon Management in the Chemical and Energy Industries

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Worldwide Chemical Industry Growth

- Driven in previous decades by materials substitution
- Products derived mostly from methane, ethane, propane, aromatics

- Likely driven in the future by GDP growth
- Supply/demand displacements are beginning to affect the relative cost and availability of some raw materials

Population and GDP Estimates

Region	2000 Pop,M	2000 pcGDP,k$	2025 Pop,M	2025 pcGDP,k$	2050 Pop,M	2050 pcGDP,k$
North America	306	30.6	370	40	440	50
Latin America	517	6.7	700	20	820	35
Europe	727	14.7	710	30	660	40
Africa	799	2.0	1260	12	1800	25
Asia	3716	3.6	4760	20	5310	35
World	6065	6.3	7800	20	9030	33

Process Industry Growth

Current North America = 1.0

Region	2000 Prod	2000-25 Growth New Plant	2000-25 Growth %Tot	2025-50 Growth New Plant	2025-50 Growth %Tot
North America	1.0	0.6	5	0.8	5
Latin America	0.4	1.1	9	1.6	10
Europe	1.1	1.1	9	0.5	4
Africa	0.2	1.5	12	3.2	21
Asia	1.4	8.2	65	9.3	60
World	4.1	12.6		15.4	

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Medium Term Economic Trends

- Much slower growth in the developed world
- Accelerating growth in the developing world
- World population stabilizing at 9-10 billion
- 6-7 X world GDP growth over next 50 or so years (in constant dollars)
- 5-6 X existing production capacity for most commodities (steel, chemicals, lumber, etc.)
- 3.5 X increase in energy demand
  - 7X increase in electricity demand

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Is such a future "sustainable"?

Sustainable Chemical Processes

- Attempt to satisfy…
  - Investor demand for unprecedented capital productivity
  - Social demand for low present and future environmental impact
- While producing…
  - Highest quality products
  - Minimum use of raw material
  - Minimum use of energy
  - Minimum waste
- In an ethical and socially responsible manner

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Sustainability Definition

"Sustainability is the path of continuous improvement, wherein the products and services required by society are delivered with progressively less negative impacts upon the Earth."

AIChE Institute for Sustainability

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AIChE Sustainability Index Components

- Environmental Performance
- Safety Performance
- Product Stewardship
- Social Responsibility
- Value-Chain Management
- Strategic Commitment

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Raw Materials

Raw Material Selection Characteristics

- Availability
- Accessability
- Concentration
- Cost of extraction (impact, resources)
- Competition for material
- Alternatives
- "Close" in chemical or physical structure
- "Close" in oxidation state

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"Oxidation States" of Carbon

- -4 Methane
- -2 Hydrocarbons, Alcohols, Oil
- -1 Aromatics, Lipids
- 0 Carbohydrates, Coal
- +2 Carbon Monoxide
- +4 Carbon Dioxide

- -2 – -0.5 Most polymers
- -1.5 – 0 Most oxygenated organics

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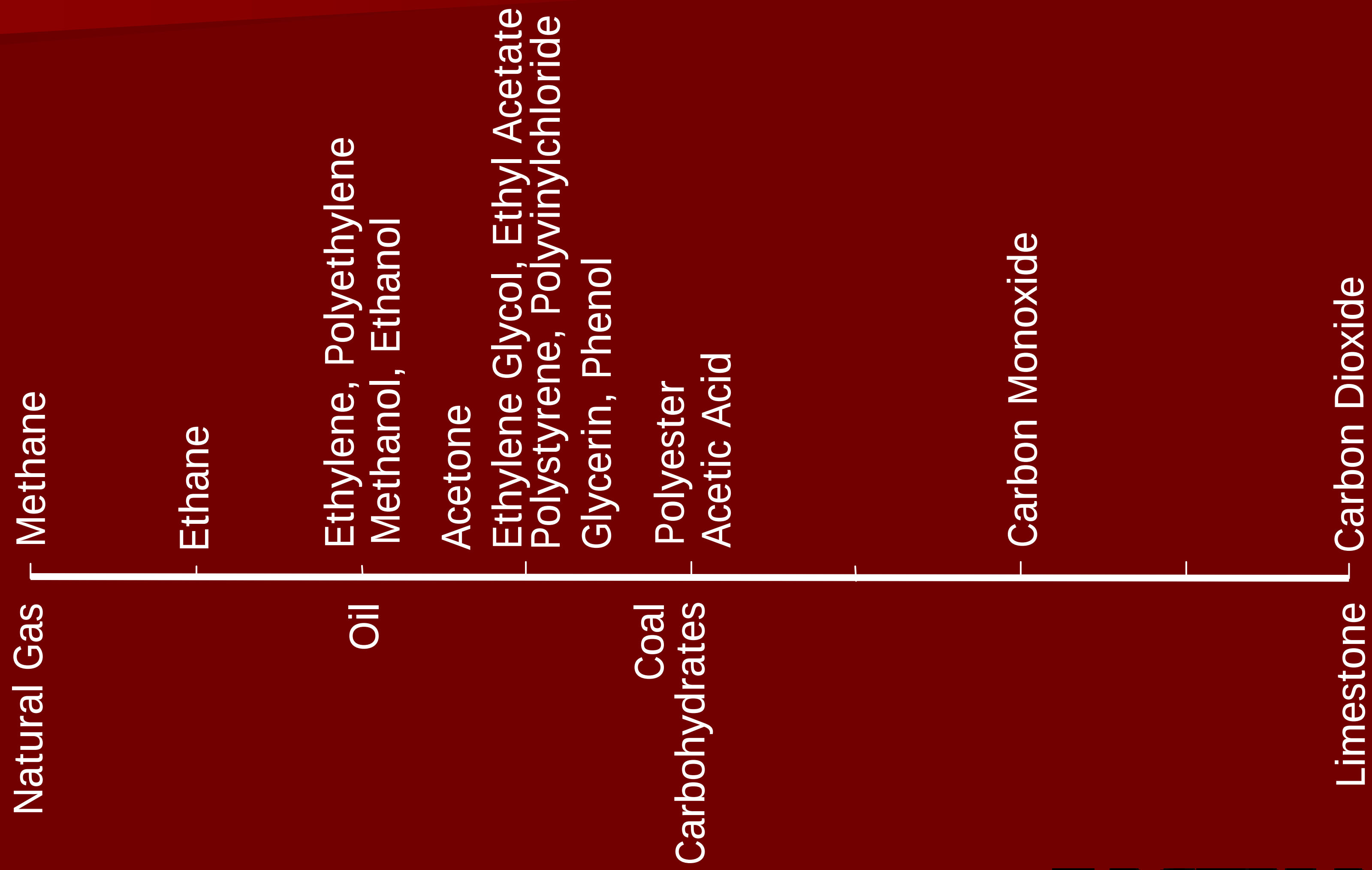
Matching Raw Material and Desired Product Oxidation States



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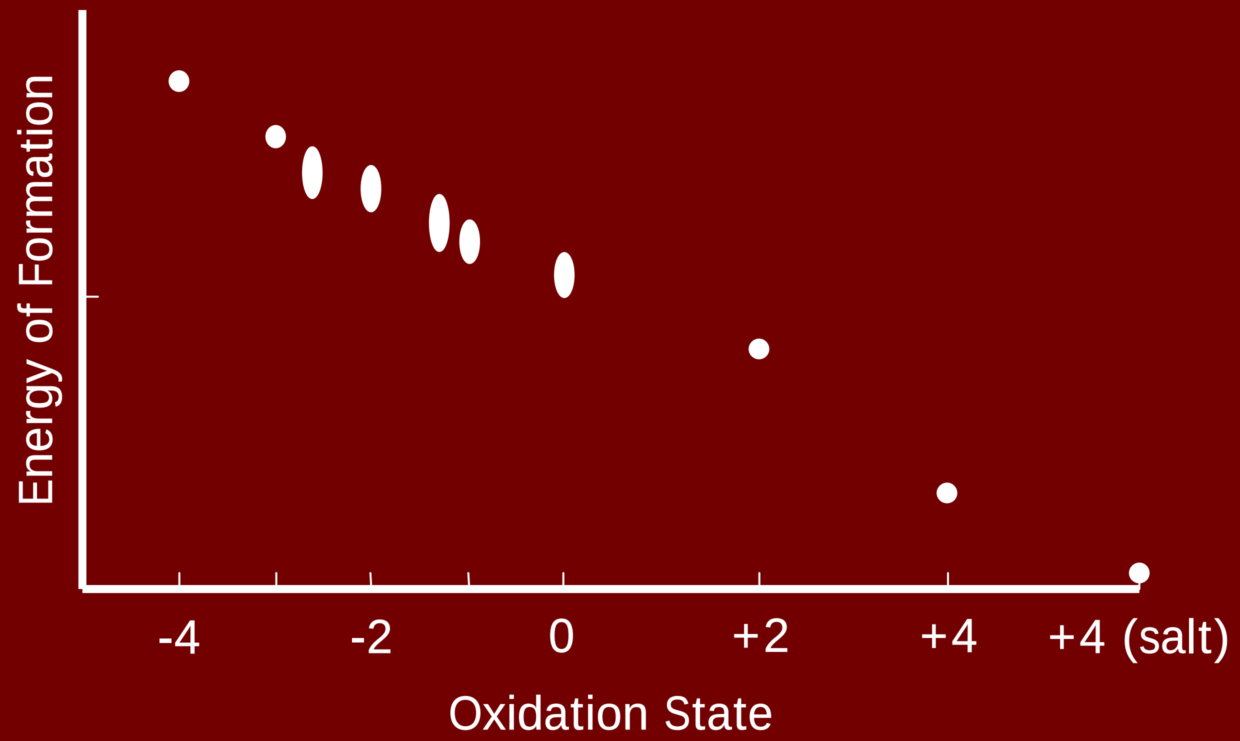
Energy and Oxidation State

Carbon



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Global Reduced Carbon

- Recoverable Gas Reserves – 75 GTC
- Recoverable Oil Reserves – 120 GTC
- Recoverable Coal – 925 GTC
- Estimated Oil Shale – 225 GTC
- Estimated Tar Sands – 250 GTC
- Estimated Remaining Fossil (at future higher price / yet-to-be-developed technology) – 2500 GTC
- Possible Methane Hydrates – ????? GTC
- Terrestrial Biomass – 500 GTC
- Peat and Soil Carbon – 2000 GTC
  - Annual Terrestrial Biomass Production – 60 GTC/yr (more than half in tropical forest and tropical savanna)
  - Organic Chemical Production – 0.3 GTC/yr

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Global Oxidized Carbon

- Atmospheric CO_2 (380ppm$_v$) – 750 GTC
- Estimated Oceanic Inorganic Carbon (30ppm) – 40000 GTC
- Estimated Limestone/Dolomite/Chalk – 100000000 GTC

If Carbon Raw Material is a Lower Oxidation State than the Desired Product

- Direct or indirect partial oxidation
  - Readily available, inexpensive ultimate oxidant
  - Exothermic, favorable chemical equilibria
  - Possible selectivity and purification issues

- Disproportionation coproducing hydrogen
  - Endothermic, sometimes high temperature
  - Generally good selectivity
  - OK if corresponding coproduct H_2 needed locally

- Carbonylation chemistry
  - CO overoxidation can be readily reversed

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If Carbon Raw Material is a Higher Oxidation State than the Desired Product

- Reducing agent typically hydrogen
- Hydrogen production and reduction reactions net endothermic
- Approximately athermic disproportionation of intermediate oxidation state sometimes possible, generally coproducing CO_2
- Solar photosynthetic reduction of CO_2 (coproducing O_2)

Industrial Hydrogen Production

- To make a mole of H_2, either water is split or a carbon is oxidized two states (or two carbons oxidized one state each)
  - Electrolysis/thermolysis
    - $H_2O = H_2 + ½ O_2$
  - Steam reforming methane
    - $CH_4 + 2 H_20 = 4 H_2 + CO_2$
  - Coal/biomass gasification
    - $C + H_2O = H_2 + CO$
    - $C(H_2O) = H_2 + CO$
  - Water gas shift
    - $CO + H_2O = H_2 + CO_2$
  - Cracking
    - $-CH_2CH_2- = H_2 + -CH=CH-$

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Matching Raw Material and Product Oxidation States / Energy

Methane
Ethane
Propane
Gasoline
Ethylene, Polyethylene
Methanol, Ethanol
Acetone
Ethylene Glycol, Ethyl Acetate
Polystyrene, Polyvinylchloride
Glycerin, Phenol
Polyester
Acetic Acid
Carbon Monoxide
Carbon Dioxide
Carbonate

Natural Gas
Condensate
Oil
Coal
Carbohydrates
Limestone

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Which is the sustainable raw material?

- The most abundant (carbonate)?
- The one for which a "natural" process exists for part of the required endothermic oxidation state change (atmospheric carbon dioxide)?
- The one likely to require the least additional energy to process into final product (oil)?
- The one likely to produce energy for export in addition to that required to process into final product (gas)?
- The one likely least contaminated (methane or condensate)?
- The one most similar in structure (perhaps biomass)?
- A compromise: abundant, close oxidation state, easily removed contaminants, generally dry (coal)?

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Energy

Current World Energy Consumption

Per Year

	Quads	Percent	GTC
Oil	150	40	3.5
Natural Gas	85	22	1.2
Coal	88	23	2.3
Nuclear	25	7	
Hydro	27	7	
Solar	3	1	

Approximately 1/3 transportation, 1/3 electricity, 1/3 everything else (industrial, home heating, etc.)

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Fossil Fuel Reserves

	Recoverable Reserves, GTC	Reserve Life @Current Rate, Yr	Reserve Life @Projected GDP Growth, Yr
Oil	120	35	25
Natural Gas	75	60	45
Coal	925	400	?

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Economic Growth Expectation

- World population stabilizing below 10 billion
- 6-7 X world GDP growth over next 50 or so years
- 5-6 X existing production capacity for most commodities (steel, chemicals, lumber, etc.)
- 3.5 X increase in energy demand
  (7 X increase in electricity demand)
- Most growth will be in the developing world

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Global Energy Demand

Quads

Region	2000	2025	2050
North America	90	100	120
Latin America	35	80	150
Europe	110	110	130
Africa	15	60	200
Asia	135	450	900
World	385	800	1500

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50-Year Global Energy Demand

- Total energy demand – 1500 Quads
- New electricity capacity – 5000 GW
  - One new world-scale 1000 MW powerplant every three days
  - Or 1000 square miles new solar cells per year
- Clean water for 9 billion people
- Carbon emissions growing from 7 GTC/yr to 26 GTC/yr
  - More, if methane exhausted
  - More, if synthetic fuels are derived from coal or biomass

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What to do with Fossil Fuels

- Based on present atmospheric oxygen, about 400000 GTC of previously photosynthetic produced biomass from solar energy sank or was buried before it had the chance to reoxidize to $CO_{2,}$ although most has disproportionated
- We can ignore and not touch them
- We can use them to make chemical products themselves stable or else reburied at the end of their lives
- We can burn them for energy (directly or via hydrogen, but in either case with rapid CO_2 coproduction)
- We can add to them by sinking or burying current biomass

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Consequences of Continuing Carbon Dioxide Emissions

- At 380ppm, 2.2 GTC/yr more carbon dioxide dissolves in the ocean than did at the preindustrial revolution level of 280ppm
- Currently, about 0.3 GTC/yr is being added to soil carbon and to terrestrial biomass due to changing agricultural and land management practices
- The balance results in ever increasing atmospheric CO_2 concentrations

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Carbon Dioxide Sequestration

- Limited options for concentrated stationary sources
  - Geologic formations (deep well, EOR, CBM)
  - Saline aquifers
  - Deep ocean hydrates
  - Alkaline (silicate) mineral sequestration
  - Alkaline (carbonate) neutralization and oceanic disposal of bicarbonate solution
- Fewer options for mobile sources
  - Onboard adsorbents
  - Photosynthesis (biofuels)
- Offset strategies
  - Enhanced oceanic or terrestrial biomass or soil carbon inventory
  - Oceanic or subterranean sequestration of terrestrial biomass

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Can We do it with Biomass?

- Current Fossil Fuel Consumption – 7 GTC/yr
- Current Chemical Production – 0.3 GTC/yr
- Current Cultivated Crop Production – 6 GTC/yr
  - Current energy crop production – 0.02 GTC/yr
- Annual Terrestrial Biomass Production – 60 GTC/yr

- Future Energy Requirement (same energy mix) – 26 GTC/yr
- Future Energy Requirement (from coal or biomass) – 37 GTC/yr
  - Plus significant energy requirement to dehydrate biomass
- Future Transportation Fuel (carbon content only) – 12 GTC/yr
- Future Chemical Demand – 1.5 GTC/yr
- Future Crop Requirement – 9 GTC/yr

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Sustainability Challenges

- Even with substantial lifestyle, conservation, and energy efficiency improvements, global energy demand is likely to more than triple within fifty years
- There is an abundance of fossil fuel sources and they will be exploited especially within developing economies
- Atmospheric addition of even a few GTC/yr of carbon dioxide is not sustainable
- In the absence of a sequestration breakthrough, reliance on fossil fuels is not sustainable
- Photosynthetic biomass is very unlikely to meet a significant portion of the projected long term energy need

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Capturing Solar Power

- Typical biomass growth rate – 400 gC/m^2/yr
  (range 100 (desert scrub) to 1200 (wetlands))
- Power density – 0.4 W_t/m^2
  (assuming no energy for fertilizer, cultivation, irrigation, harvesting, processing, drying, pyrolysis)

- Average photovoltaic solar cell power density – 20-40 W_e/m^2
  (10% module efficiency, urban-desert conditions)

- Solar thermal concentration with Stirling engine electricity generation is another possibility at 30% efficiency

- Because of limited arable land, available water, harvesting resources, and foodcrop competition, biomass may not be an optimal method to capture solar energy

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Solar Energy Storage Options

- In atmospheric pressure gradients (wind) and terrestrial elevation gradients (hydro)
- In carbon in the zero oxidation state (biomass or coal)
- In carbon in other oxidation states (via disproportionation, digestion, fermentation)
- In other redox systems (batteries)
- As molecular hydrogen
- As latent or sensible heat (thermal storage)

The Hydrogen Option

- Potentially fewer pollutants and no CO_2 production at point of use
- Fuel cell efficiencies potentially higher than Carnot-limited thermal cycles

- No molecular hydrogen available
- Very low energy density
- Very difficult to store
- Consumer handling issues
- An energy carrier, not an energy source

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Hydrogen Production

- If from reduced carbon, then same amount of CO_2 produced as if the carbon were burned, but potential exists for centralized capture and sequestration
- Could come from solar via (waste) biomass gasification, thermal or photochemical water splitting, or photovoltaic or thermoelectric driven electrolysis

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Energy Carriers and Systems

- For stationary applications: electricity, steam, town gas, and DME from coal, natural gas, fuel oil, nuclear, solar, hydrogen
  - Electricity generation and use efficient, but extremely difficult to store
  - Battery or fuel cell backup for small DC systems
  - CO_2 sequestration possible from large centralized facilities
- For mobile (long distance) applications: gasoline/diesel, oil
  - Electricity for constrained routes (railroads) only
  - Hydrogen is also a long term possibility
- For mobile (urban, frequent acceleration) applications: gasoline/diesel, alcohols, DME
  - Vehicle mass is a dominant factor
  - Narrow internal combustion engine torque requires transmission
  - Disadvantage offset and energy recovery with hybrid technology
  - Highest energy density (including containment) by far is liquid hydrocarbon
  - Capturing CO_2 from light weight mobile applications is very difficult

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Conclusions

- By a factor of 10^5, most accessible carbon atoms on the earth are in the highest oxidation state
- However, there is plenty of available carbon in lower oxidation states closer to that of most desired chemical products
  - High availability and the existence of photosynthesis does not argue persuasively for starting from CO_2 or carbonate as raw material for most of the organic chemistry industry
  - But, the same might not necessarily be true for the transportation fuels industry, especially if the energy carrier is carbonaceous but onboard CO_2 capture is not feasible

Conclusions

- Inexpensive natural gas, condensate, and oil will become depleted
- With enough capital, can get to any carbon oxidation state from any other, but reducing oxidation state costs energy
- There will be a shift to higher oxidation state starting materials including coal and biomass for chemical and fuel production, with corresponding increases in CO_2 generation
- Sequestration innovations will be essential

The Chemical Industry

- Most new chemical capacity will be built near the customer (except when the raw material is stranded gas)
- Some new processes will be built to substitute for declining availability of natural gas, condensate, and aromatics
- Some new processes will be built implementing new routes to intermediates currently derived from methane, olefins, and aromatics
- Catalysis, process chemistry, and process engineering innovations will be critical

The Energy Industry

- Again, there will be a shift to higher oxidation state starting materials for energy production with corresponding increases in CO_2 generation

- Significant new capacity will be built for synthetic fuels

- In the long term, solar, nuclear, and geothermal energy will be employed to produce electricity and may be employed to produce hydrogen for fuel use directly or for reaction with atmospheric CO_2 to produce a more convenient carbonaceous fuel

- Within 50 years, the size of the global synthetic fuel infrastructure may very well be more than three times the entire existing petroleum-based fuel infrastructure (over 200 times the entire existing US chemical industry)

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Break

Carbon Management

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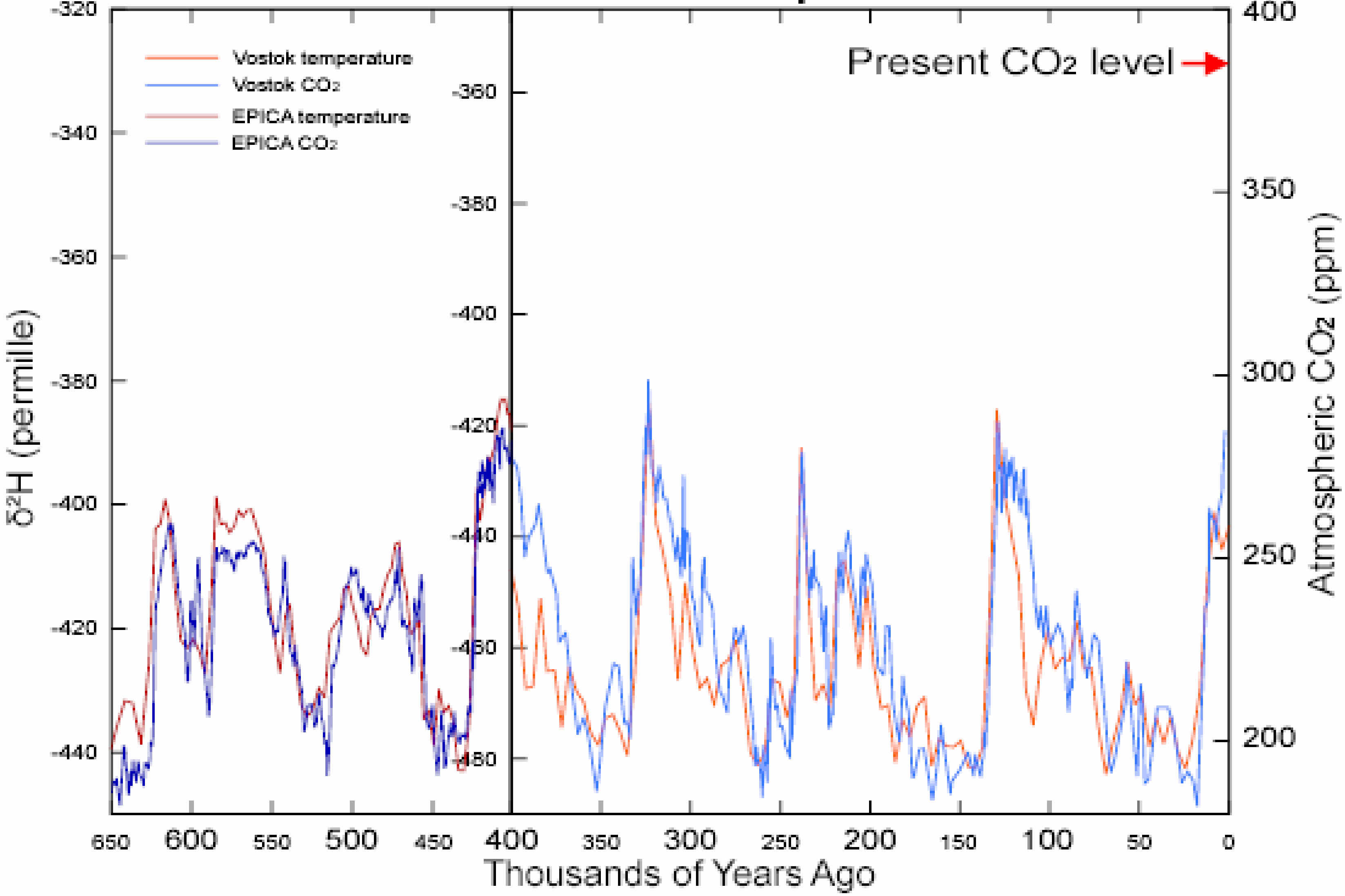
Carbon Dioxide and Temperature Records



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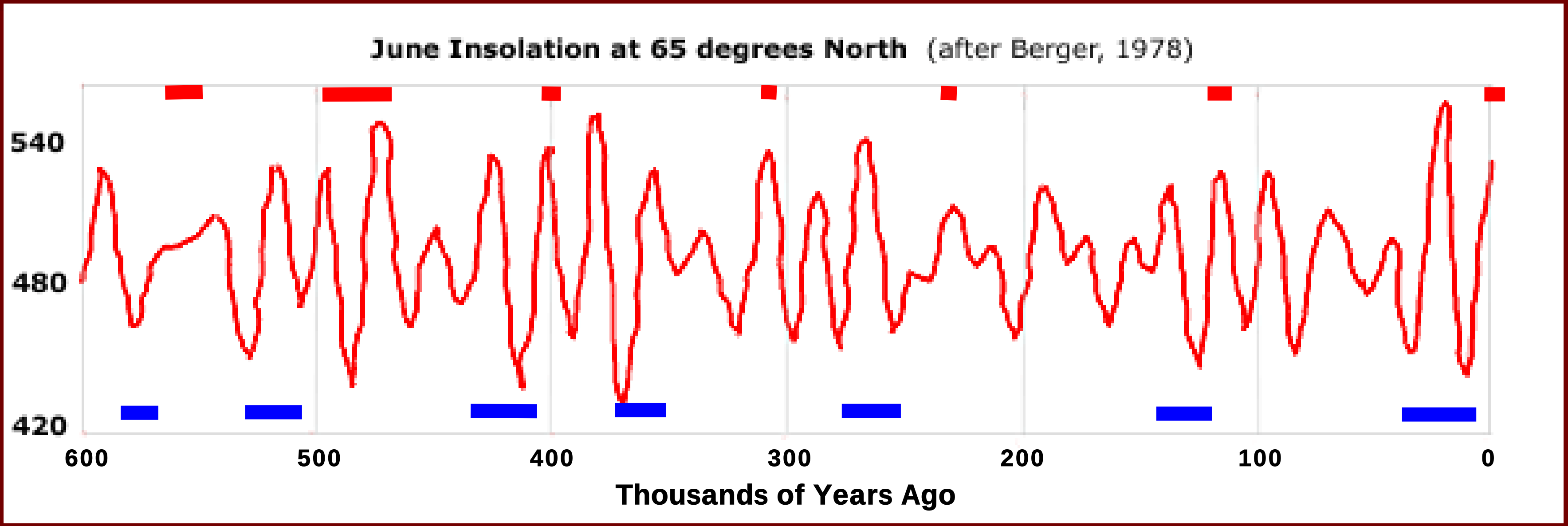
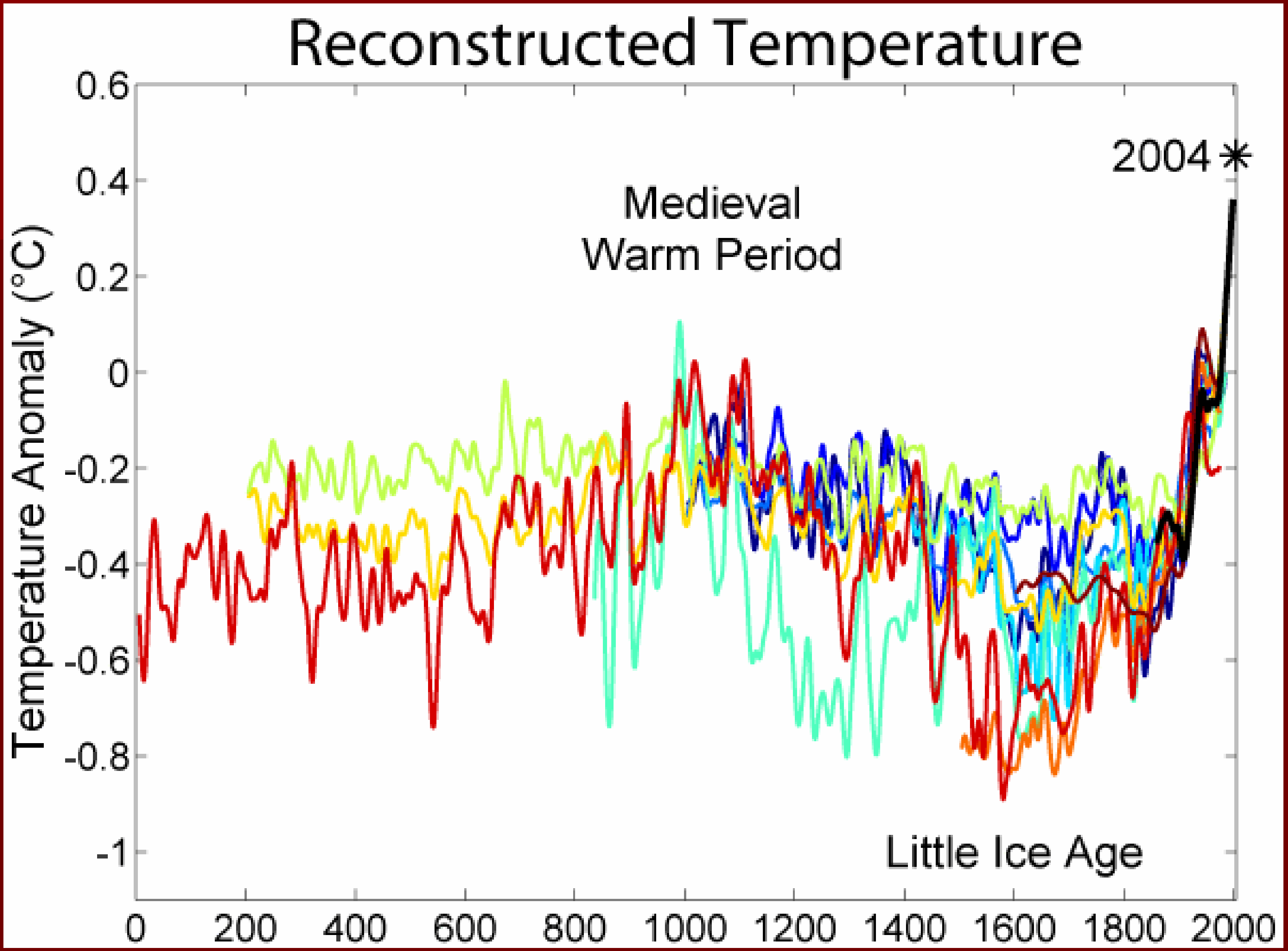

June Insolation at 65 degrees North (after Berger, 1978)
540
480
420
600
500
400
300
200
100
0
Thousands of Years Ago



Reconstructed Temperature
Temperature Anomaly (°C)
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2004
Medieval Warm Period
Little Ice Age

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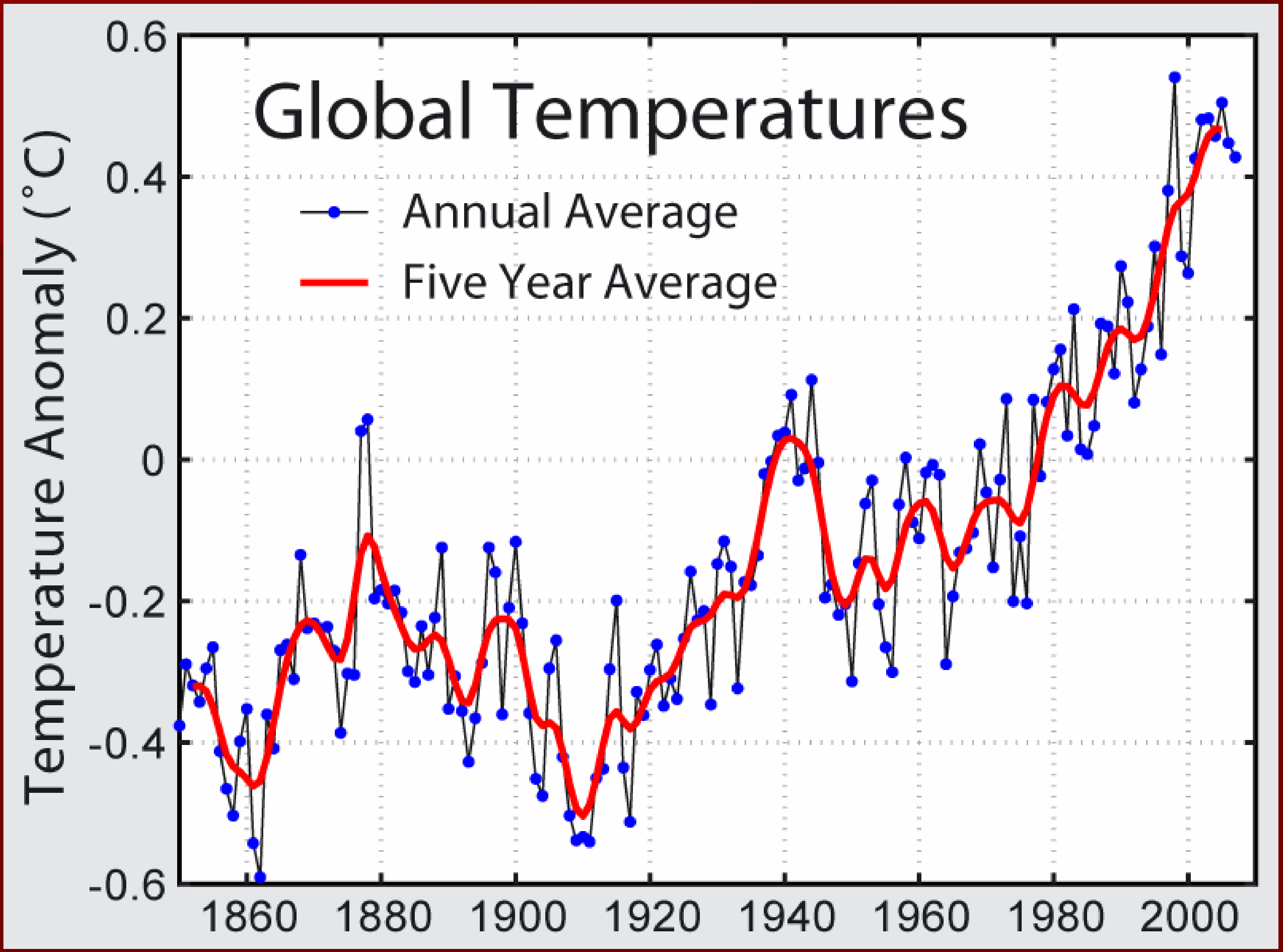

Global Temperatures
Annual Average
Five Year Average
Temperature Anomaly (°C)
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
1860
1880
1900
1920
1940
1960
1980
2000

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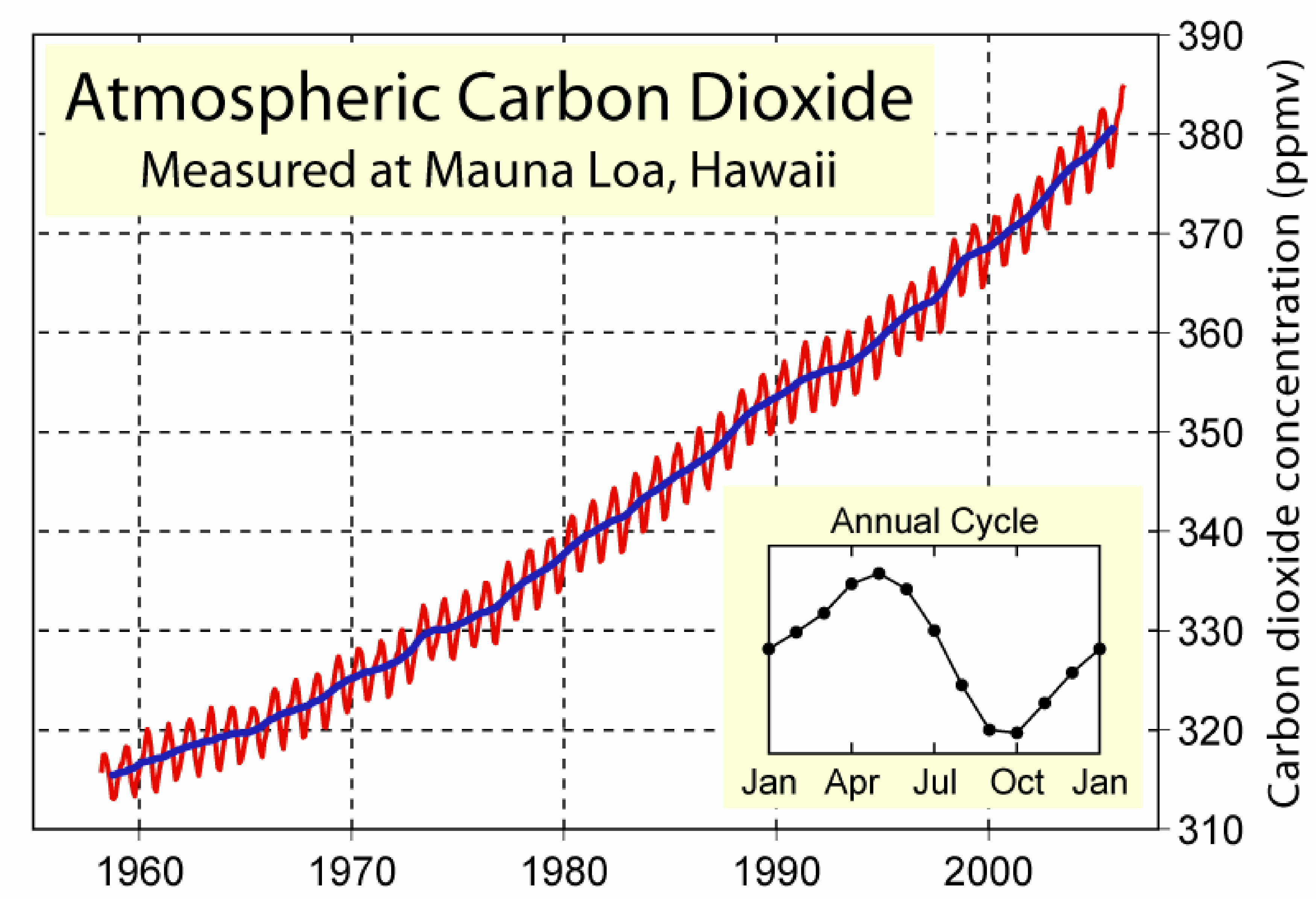

Atmospheric Carbon Dioxide
Measured at Mauna Loa, Hawaii
390
380
370
360
350
340
330
320
310
Carbon dioxide concentration (ppmv)
1960
1970
1980
1990
2000
Annual Cycle
Jan
Apr
Jul
Oct
Jan

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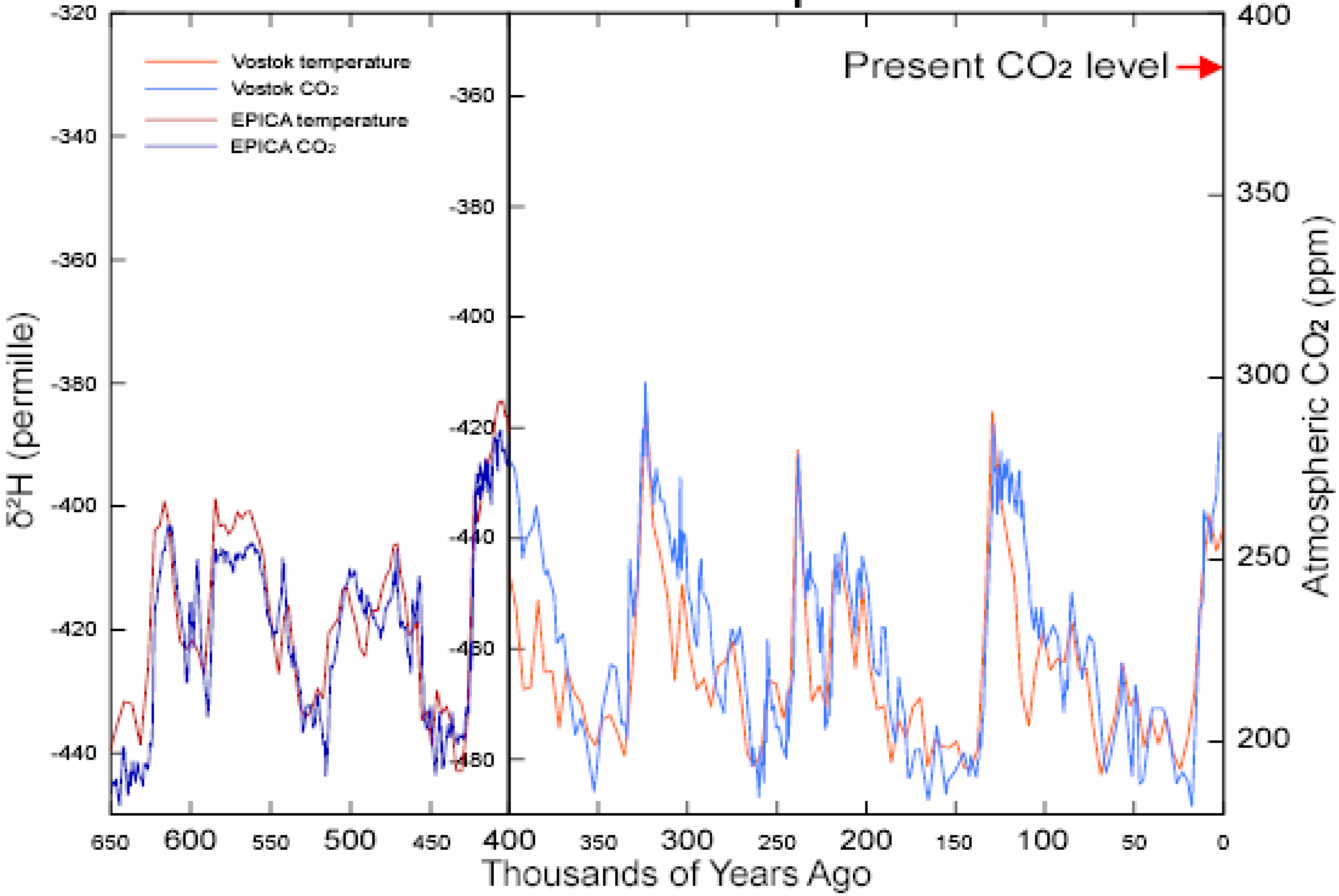
Carbon Dioxide and Temperature Records



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Approaches to Carbon Management

- Reduce Carbon Dioxide Production
- Offset Carbon Dioxide Production
- Carbon Dioxide Collection
- Carbon Dioxide Storage

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Reduce Carbon Dioxide Production

1. Reduce energy usage
   a. Produce less product (change product portfolio)
   b. Decrease energy use per unit of production (process improvement)
   c. Recover and reuse energy (process intensification and heat integration)

2. Switch to a more energy-intense fossil source for fuel and feedstock
   a. Switch from oil to gas
   b. Switch from coal to oil or gas

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Reduce Carbon Dioxide Production

Continued

3. Use non-carbonaceous energy sources
   a. Nuclear
   b. Solar-hydroelectric
   c. Solar-wind
   d. Solar-photovoltaic
   e. Solar-thermal
   f. Geothermal
   g. Wave
   h. Tidal

4. Change reaction chemistry to produce less carbon dioxide

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Offset Carbon Dioxide Production

1. Burn fossil fuel and harvest and bury/sink an equivalent amount of biomass

2. Cultivate (crop), recover (residues), or recycle (waste) biomass for fuel and feedstock
    a. Burn biomass directly for heat and power
    b. Biologically or chemically convert biomass to alternative fuel (e.g., bioethanol, biobutanol, or biodiesel)
    c. Pyrolyze/gasify biomass and convert to alternative fuel
    d. Convert biomass into chemical feedstock

3. Convert recovered carbonaceous wastes into fuel or feedstock

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Offset Carbon Dioxide Production
Continued

4. Sell carbon dioxide or a carbon dioxide derivative for any permanent use

5. Chemically reduce carbon dioxide to lower oxidation state
   a. Reform carbon dioxide with methane to syngas
   b. Reduce carbon dioxide collected from processes, flues, or the atmosphere with waste hydrogen or hydrogen produced from nonfossil energy (nuclear, solar, geothermal) into fuel and feedstock

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Carbon Dioxide Capture

1. Collect from dilute point sources – fluegas scrubbing
    a. Alcoholamines
    b. Chilled ammonia
    c. Caustic or lime
    d. Carbonate
    e. Enzymatic liquid and active transport membranes

2. Collect from concentrated point sources – gasifier acid gas removal
    a. Rectisol (cold)
    b. Selexol (warm)
    d. Metal oxides (hot)

3. Collect from virtually pure sources
    a. Oxygen-fired furnaces, kilns, or turbines (oxyfuel)
    b. Fully shifted syngas (hydrogen fuel)

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Carbon Dioxide Capture

Continued

4. Collect from mobile sources
    a. Lithium hydroxide

5. Collect from atmosphere by scrubbing
    a. Caustic
    b. Metal oxides
    c. Unknown optimized reactive sorbent

6. Collect from atmosphere by growing biomass
    a. Cultivated crops, forest plantations, aquatic species
    b. Natural diverse vegetation and forest products

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Carbon Dioxide Storage

1. Deep well codisposal with H_2S, SO_x or NO_x

2. Geologic (as pressurized gas, liquid, or carbonic acid; +4 oxidation state)
   a. Porous capped rock (with or without oil recovery)
   b. Coal beds (with or without methane displacement)
   c. Saline aquifer

3. Oceanic (+4 oxidation state)
   a. Ocean disposal (as carbonic acid)
   b. Deep ocean disposal with hydrate formation
   c. Ocean disposal with limestone neutralization (as bicarbonate solution)

4. Land disposal as carbonate salt (+4 oxidation state)
   a. Reaction with silicate

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Carbon Dioxide Storage
Continued

5. Ocean sinking of biomass (0 oxidation state)
   a. Fertilized ocean (iron or nitrogen)
   b. Cultivated terrestrial biomass (crops, grasses, trees, algae)
   c. Uncultivated terrestrial biomass

6. Land burial of biomass (0 oxidation state; augment soil carbon)
   a. Terrestrial burial of cultivated biomass and residues
   b. Terrestrial burial of uncultivated biomass

7. Land burial of recovered biomass and chemical products
   a. Used paper and lumber products
   b. Waste municipal biomass
   c. Recycled scrap or used chemical products (e.g., polymers)

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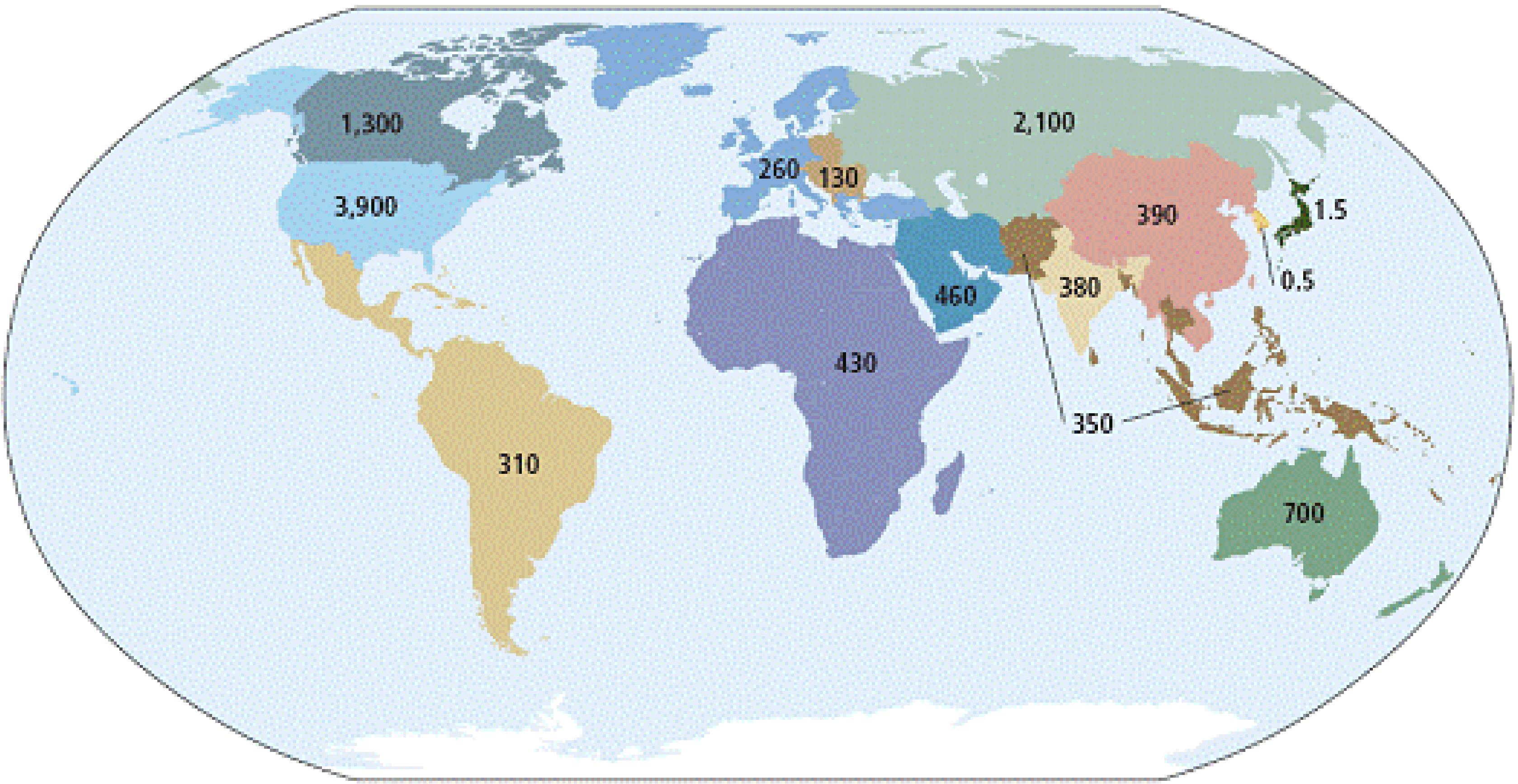
Estimated world wide CO_2 storage options

FIGURE 8: GLOBAL CO_2 STORAGE CAPACITY (GIGATONS)



Initial assessments of theoretical global CO_2 storage capacity reveal an important and encouraging result: there is more than enough theoretical CO_2 storage capacity in the world to meet likely storage needs for at least a century, and in many key regions the storage capacity is in the right places to meet current and future demand from nearby CO_2 sources.

Source: Battelle Climate Research Institute, *Carbon Dioxide Capture and Geological Storage*, April 2006.

Most Likely Options

Reduce carbon dioxide production

Switch to more energy-intense fossil sources

Reduce energy usage

Use non-carbonaceous energy sources

Change reaction chemistry

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Most Likely Options

Offset carbon dioxide production

- *Convert biomass to fuel*
- *Bury/sink equivalent biomass*
- Convert wastes to fuel
- Chemically reduce carbon dioxide
- Sell carbon dioxide derivative

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Most Likely Options

Carbon dioxide capture

Concentrated point sources
Dilute point sources
Grow biomass
Pure sources
Atmospheric scrubbing
Mobile sources

Most Likely Options

Carbon dioxide storage

EOR, CBM, and saline aquifer
Land burial of biomass
Ocean sinking of biomass
Deep ocean disposal
Land burial of recovered products
Deep well injection
Carbonate salt

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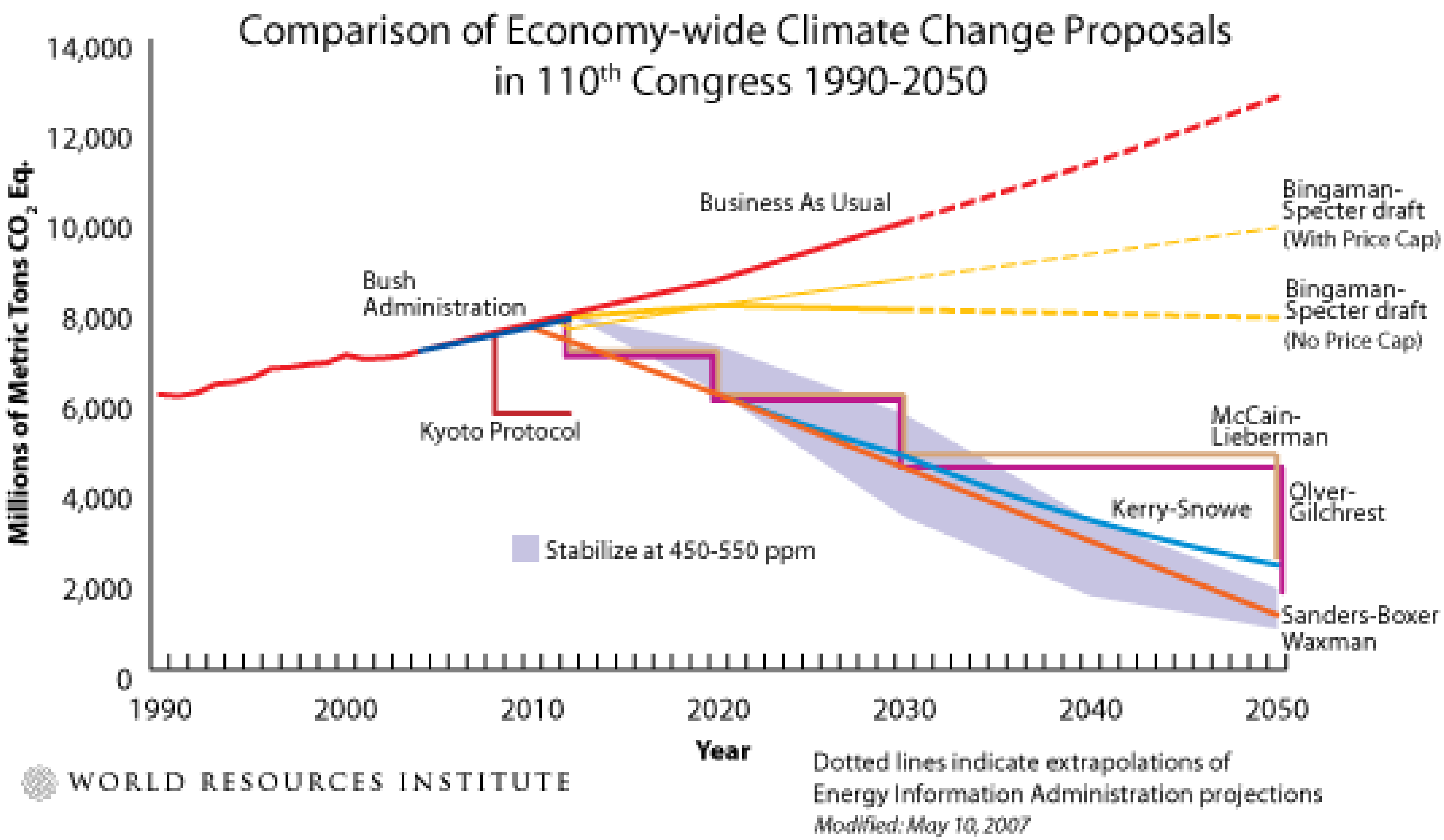
Impacts of proposed US GHG legislation if enacted in 2007



http://www.wri.org/climate/topic_content.cfm?cid=4265

Addendum

A Roadmap to Chemical and Energy Sustainability

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Sustainability Roadmap
Immediate

- 1. Conserve, recover, reuse

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Sustainability Roadmap
Immediate

- 2. Reevaluate expense/investment optimizations in light of fundamental changes in relative feedstock availability and cost and capital/energy relationships

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Sustainability Roadmap
Short Term

- 3. For fuels, develop economically justifiable processes to utilize alternative fossil and biological feedstocks. Develop refining modifications as necessary to process feedstocks with alternative characteristics. Develop user (burner, vehicle, distribution, storage, etc) modifications as necessary to adapt to differences experienced by the ultimate consumer.

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Sustainability Roadmap
Short Term

- 4. For organic chemicals, develop economically justifiable processes to utilize alternative feedstocks. Develop processes to make first-level intermediates from alternative feedstocks. Develop processes to make second-level intermediates from alternative first-level intermediates (from alternative feedstocks).

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Sustainability Roadmap
Intermediate Term

- 5. For fuels and used organic chemicals that are burned/incinerated at a stationary site, develop, evaluate, and implement alternative processing, combustion, carbon dioxide capture, and carbon dioxide sequestration technologies

Sustainability Roadmap
Intermediate Term

- 6. For transportation fuels and dispersed heating fuels, consider stationary conversion of coal or biomass to lower oxidation state carbonaceous energy carriers with resulting coproduct carbon dioxide recovery and sequestration, as above

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Sustainability Roadmap
Intermediate Term

- 7. For transportation fuels and dispersed heating fuels, consider stationary conversion of carbonaceous materials to non-carbon energy carriers with coproduct carbon dioxide recovery and sequestration, as above

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Sustainability Roadmap
Intermediate Term

- 8. For carbonaceous energy carriers and dispersed organic chemicals, grow and harvest an offsetting amount of biomass for either feedstock or burial. Develop geographically appropriate species optimized (yield, soil, water, fertilization, cultivation, harvesting, processing requirements (including water recovery), disease and pest resistance, genetic diversity, ecosystem interactions, etc) for this purpose.

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Sustainability Roadmap
Intermediate Term

- 9. Exploit nuclear (and geothermal) energy for electricity generation and industrial heating uses

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Sustainability Roadmap
Intermediate Term

- 10. Exploit hydro, wind, and solar photovoltaic for electricity production and solar thermal for electricity production, domestic heating, and industrial heating uses

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Sustainability Roadmap
Intermediate Term

- 11. Exploit solar or nuclear energy to produce hydrogen to reduce biomass or coal to lower oxidation state forms and to process into carbonaceous fuels

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Sustainability Roadmap
Intermediate Term

- 12. Exploit solar and nuclear energy chemically or biochemically to reduce carbon dioxide (recovered from carbonaceous burning or coproduct from oxidation state reduction operations) into lower oxidation state forms for sequestration or reuse as carbonaceous energy carriers and organic chemicals

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Sustainability Roadmap
Long Term

- 13. Develop non-biological atmospheric carbon dioxide extraction and recovery technology with capacity equal to all disperse carbon dioxide emissions from fossil fuel combustion (for transportation or dispersed heating) and from used organic chemicals oxidation (from incineration or biodegradation)

Sustainability Roadmap
Long Term

- 14. Convert carbon dioxide extracted from the atmosphere to carbonaceous energy carriers and organic chemicals with water and solar-derived energy (utilizing thermal and/or electrochemical reactions)

Thank You

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