# “Electrochemical reduction of $CO_2$ for the production of synthetic fuels”

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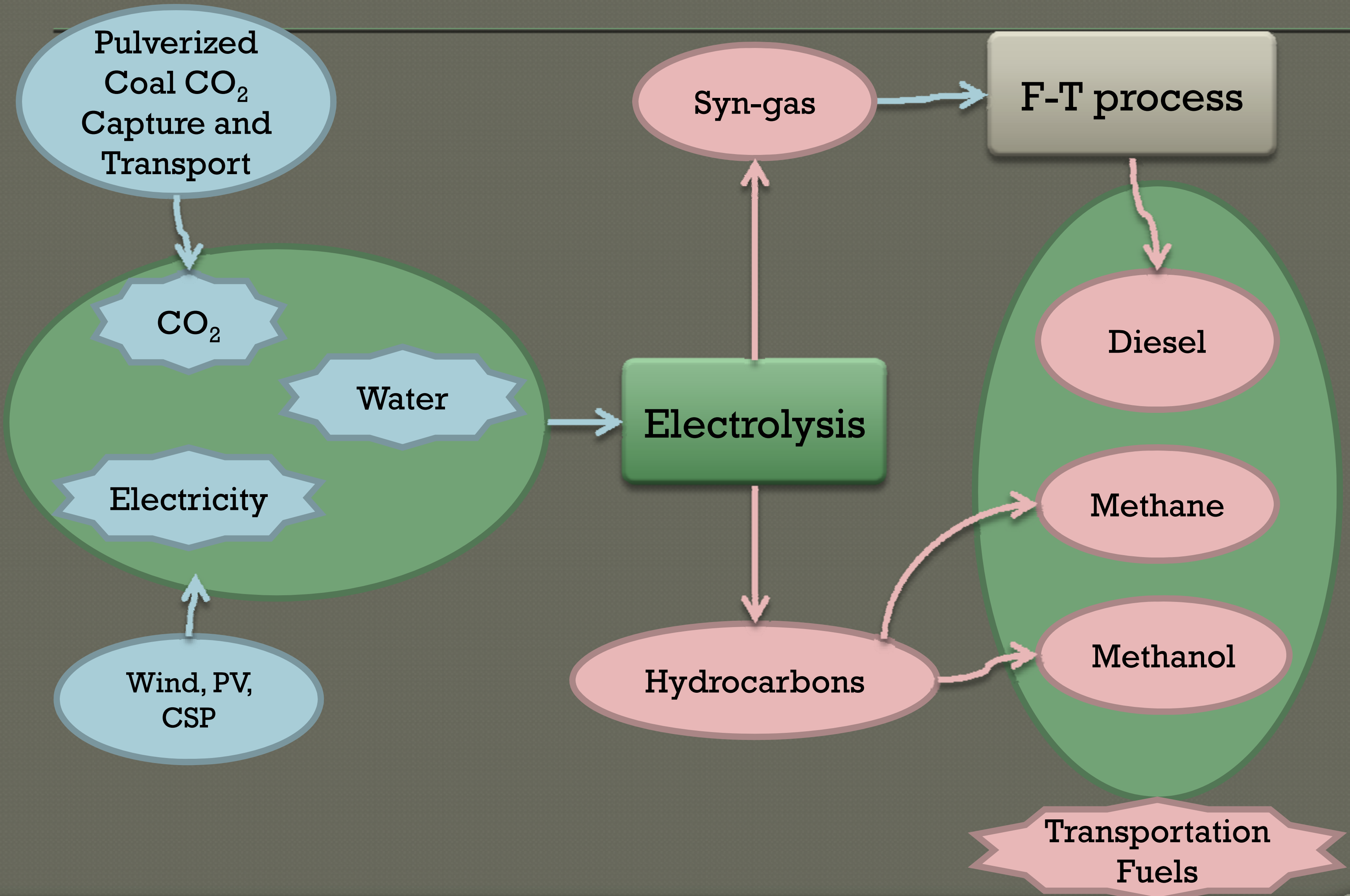
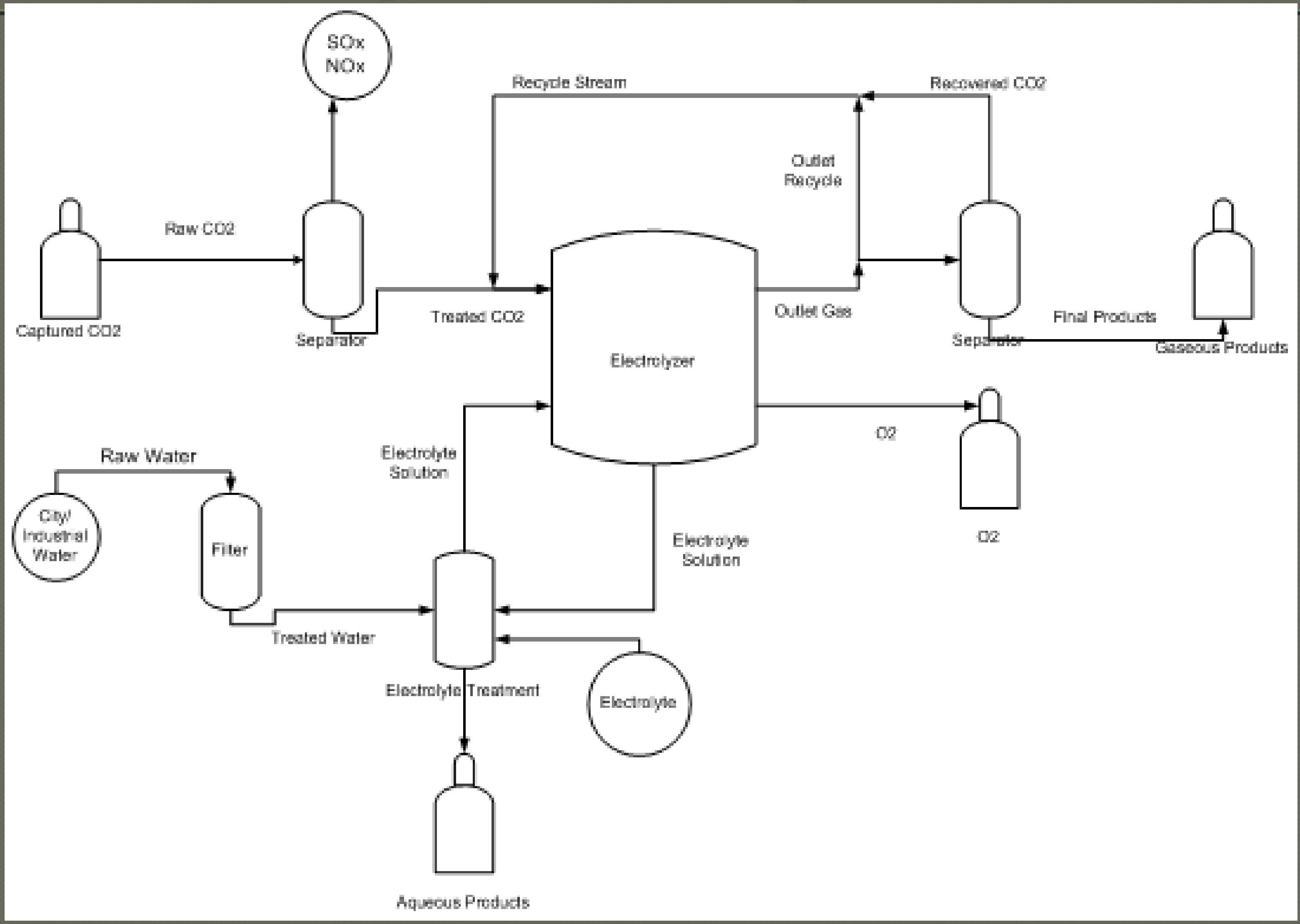
# Project Goals

- Propose electrochemical system for converting $CO_2$ to portable fuels
- Perform economic analysis for process
- Compare results and potential to some storage alternatives

# Team Concept Map



# System Layout



# System Breakdown

- Inputs
  - $CO_2$ from capture and sequestration
    - Coal fired plant
  - Water from city/industrial source
  - Excess electricity from renewable sources or off-peak grid

# System Breakdown

- Outputs
  - Hydrocarbons
    - Methanol
    - Methane
    - Formic acid
    - Ethylene
  - Syngas
  - Oxygen
  - Hydrogen

# System Components

- Electrolysis cell
  - Cathode catalysts: Ni, Cu, TiO2/RuO2, Cu/Zn/Al alloy
  - Anode catalysts: same as standard electrolyzers
  - Electrolyte: KHCO3, NaHCO3, Buffer solutions, Li salt; Aqueous and methanol
  - Membrane: ion exchange membrane (cation or anion exchange)
- Electrolyte treatment

# System Components

- Input separation
  - Impurities (SOx/NOx) from CO2
    - Not present in standard electrolyzers
  - Water filtration
    - Standard for electrolysis

# System Components

- Gaseous products
  - Will likely require recycle stream
  - Non-recycled products will require removal of $CO_2$ and final separation
  - Likely to use membrane separation
  - $O_2$ will be pure (after removal of water vapor) and can be stored directly
  - Syngas will require little to no processing

# System Components

- Liquid products
  - Require removal from electrolyte solution
  - Methanol would likely be distilled
    - Would need concentration on order of 100 mM to equal energy required to boil 1 kg of solution
    - Currently on order of 10 mM (Bandi 1990)
  - Formic acid would also require removal
  - Processing would still require control of electrolyte before re-entering the cell

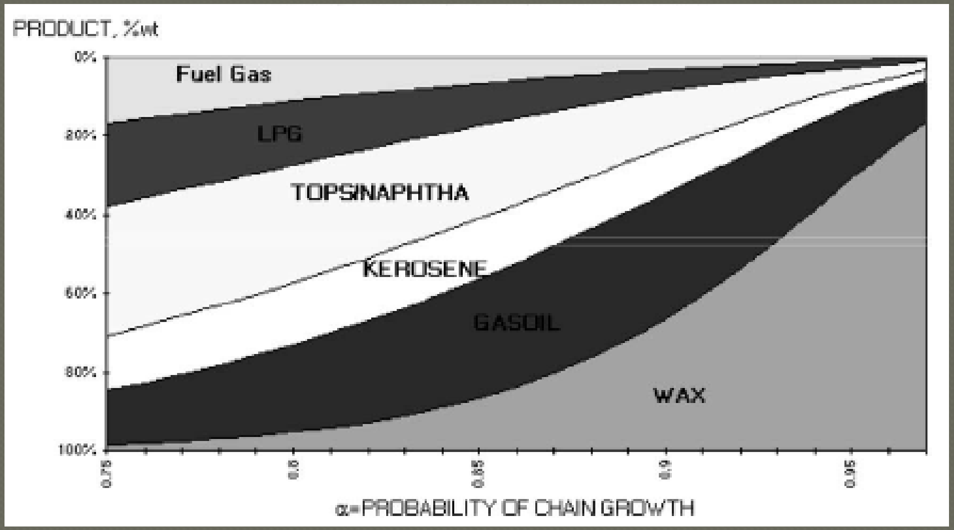
# F-T Diesel Justification

- Efficiency
  - 33% efficiency increase over gasoline engines
    - 26.6 mpg instead of 20 mpg for SUV
    - 39 mpg average for light-duty diesel vehicle.
- Emissions Reductions
  - Advanced diesel engines contain diesel particulate filters and $NO_x$ traps.
- Energy Density
  - 8% decrease of F-T Diesel to petroleum diesel, accounted for in $CO_2$ mitigation calculations.

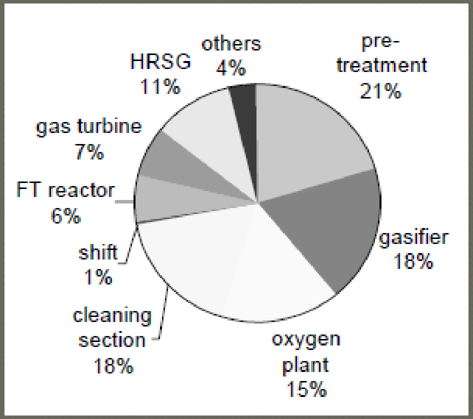
# F-T Liquids Synthesis

Anderson-Shulz-Flory Chain Growth Probability

$$C_n = \alpha^{n-1}(1-\alpha)$$




F-T Reactor only 6% of total capital cost of Coal to Liquids refinery



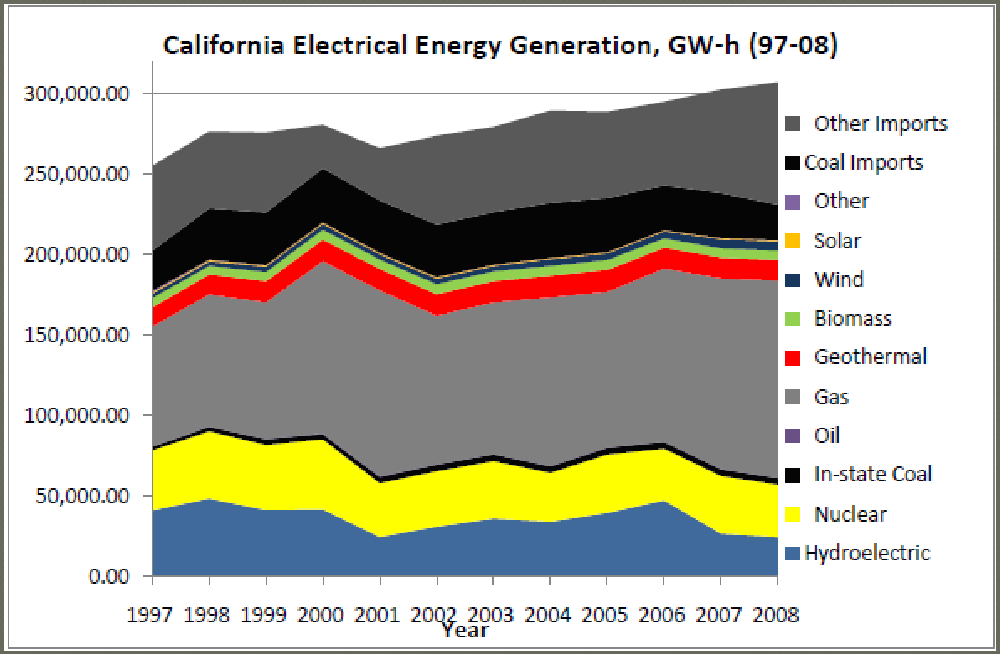
# F-T Reactor

- F-T Reactor Parameters
  - Fixed bed slurry with Co catalyst
  - 35 bar
  - Single pass
  - Chain growth probability – 0.8
    - $S_{C5+} = 78\%$
  - C1-C4 hydrocarbons sold as off-gas or used in gas turbine.

| Product split | Gasoil mode (%) |
|---|---|
| Naphtha | 15 |
| Kerosene | 25 |
| Gasoil (diesel) | 60 |

# California Electrical Energy

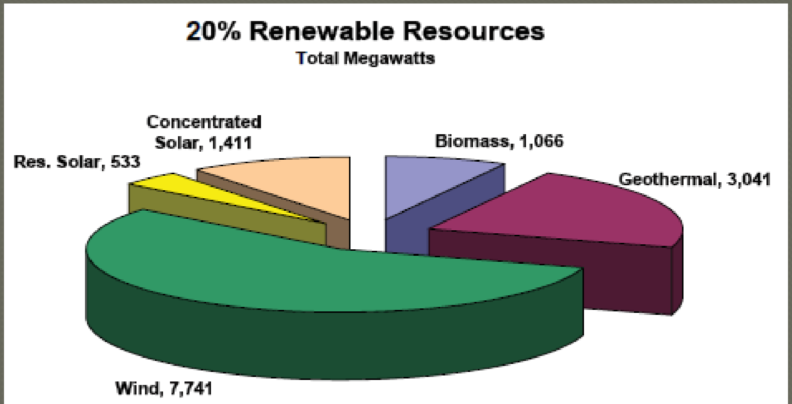
- 45.7% of electricity produced from natural gas.
- Total of 306,000 GW-h in 2008

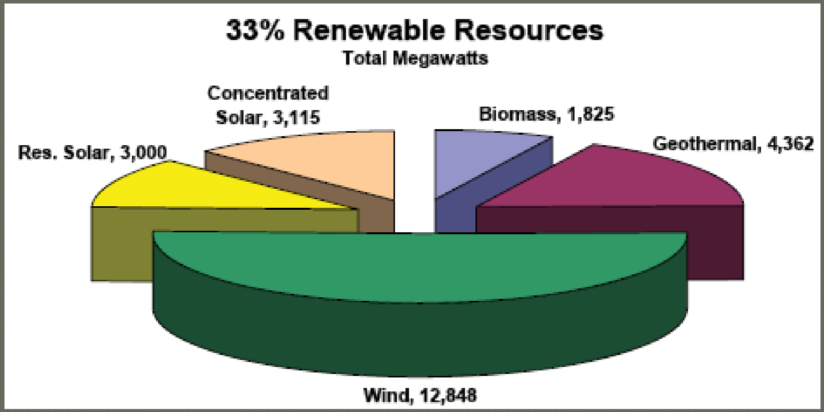


# California's Renewable Energy Initiative

**California's 2010 20% RPS goal achieved**

•Currently the variability of wind and solar generated energy production from a small number of units is usually much less than the variability of system load changes.




**California's 2020 33% RPS Goal**

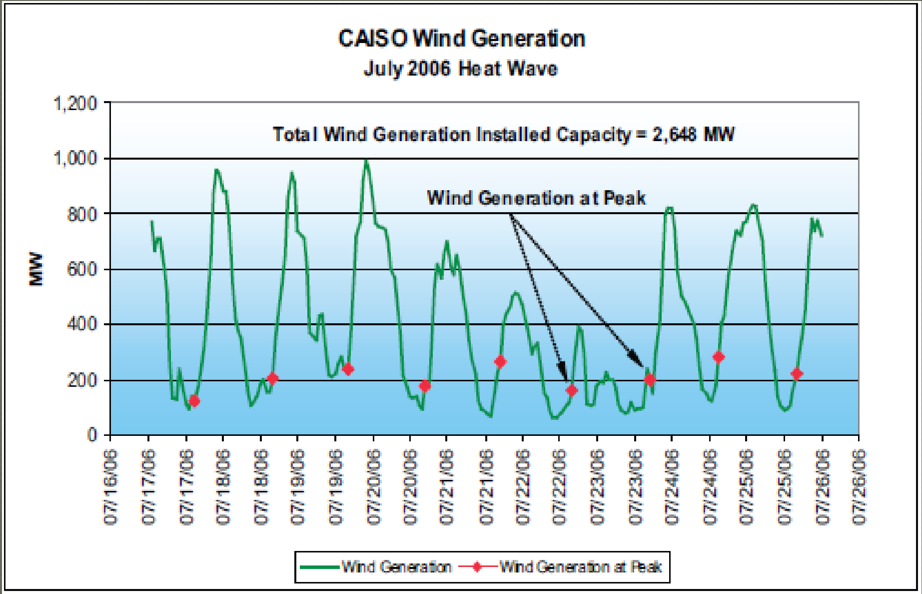
•The amount of variability increases non-linearly.

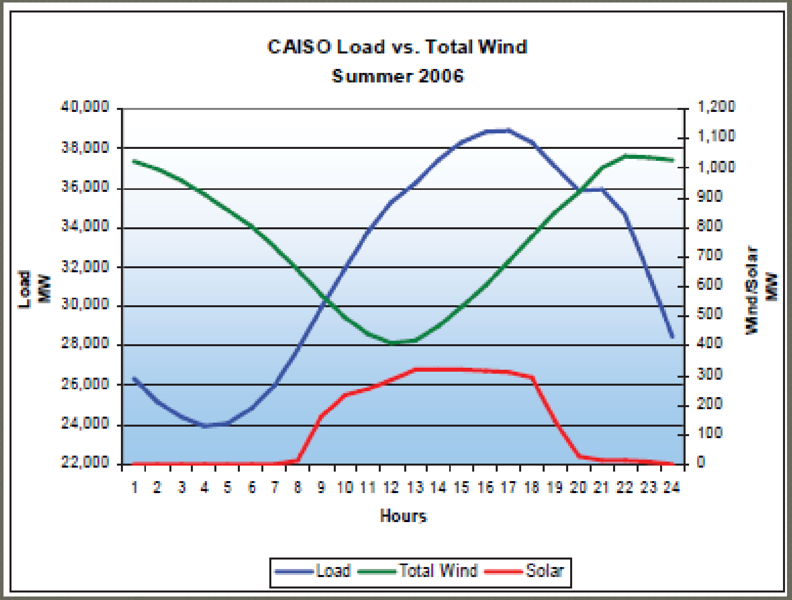
•The 33% RPS goal could more than double integration problems and costs.

•Intermittent renewable energy capacity value is ~30%, thus for every 100 MW of installed capacity only 30 MW will be achieved yearly.

# Wind vs. Load Peak Matching

Short and fast start facilities need to ramp up approx. 12.6 GW in the morning (2 hr) and ramp down 13.5 GW in the evening (3 hr) which is exuberated by non-coincident peak of wind energy.



# Energy Storage

- Types
  - Pumped Hydro Storage
  - Compressed Air Energy Storage
  - Batteries
  - Hydrogen
  - Plug in EV (V2G)
  - $CO_2$ Electrolysis
- Benefits
  - Mitigate over-generation.
  - Mitigate large ramps.
  - Transfer off-peak power to on-peak power.
  - **Match system load with off-peak power.**
- Drawbacks
  - Highly capital intensive. (Normally 1 – 1.5 MM$ / MW capacity)
  - Investors usually do not see necessity of energy storage for renewable energy induction.
  - Efficiency loss
  - PHS and CAES use geographic land features and are therefore site specific.

# Energy Storage Efficiency, Capital and Capacity

| Energy Storage Type | Cycle Efficiency | Capacity (MW) | Capital ($/kW) |
|---|---|---|---|
| PHS | 0.65-0.8 | 1000-3000 | 500-1500 |
| CAES | 0.4-0.5 | 200-500 | 250-1000 |
| Hydrogen | 0.4-0.6 | 100 | 800 |
| Lead-Acid | 0.7-0.8 | 40-100 | |
| Lithium-ion | 0.7-0.9 | 200 | 600 |
| Flywheel | 0.8-0.95 | 20-40 | 100-300 |

# $CO_2$ Electrolysis as Alternative

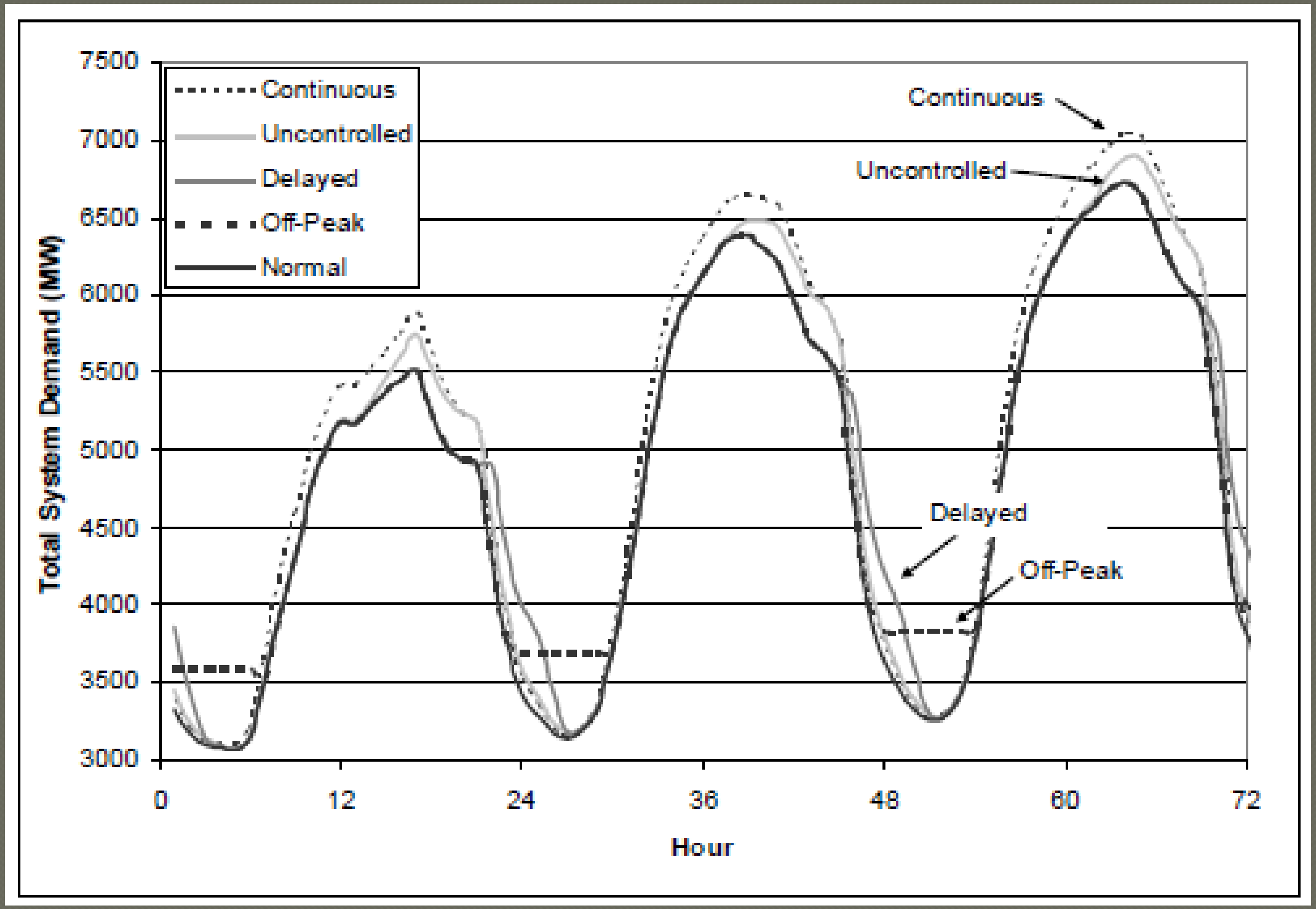
- Assist with the induction of intermittent renewable electricity without energy storage investments.
- Stand-alone unit functioning with off-grid renewable power.

| Product | Conversion Efficiency (%) |
|---|---|
| Methane | 12.2 |
| Methanol | 48.81 |
| H2:CO - 2:1 | 47.26 |
| F-T Diesel | 36.8 |

# Plug-in Electric Vehicles as Alternative

- Batteries of EV could be used as an energy storage source (V2G)
  - 9-10 kW-h = 1 gal. gasoline
- Advantages
  - Balance fluctuations in load.
  - Save $200-450/yr in energy cost when charged off-peak.
- Disadvantages
  - Increase home transformer and feeder capacity
  - Several regulations required as to when battery systems can be charged to prevent grid overloading.

# PHEV System Load

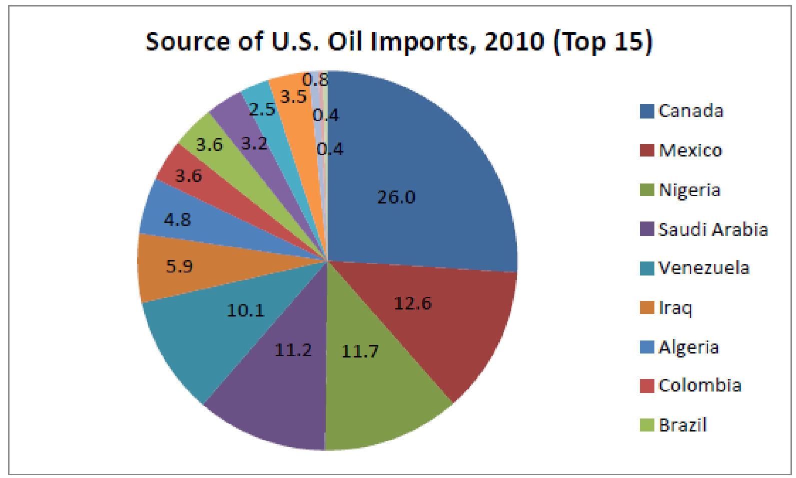


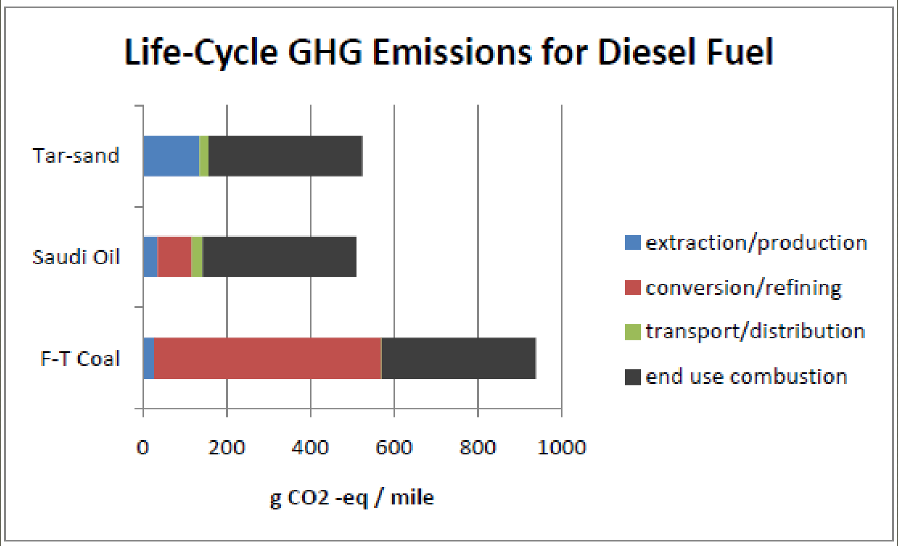
# Estimation of Excess Energy for $CO_2$ Electrolysis and/or EV

- Little excess energy available in 2010 scenario (500 MW for 100 hours/year)
- Very high over-generation anticipated for 33% renewable integration.
- 2.8 – 3.3 c/kW-h off-peak currently. (CAISO)

# $CO_2$ Emissions Mitigated

- Since the majority of oil imports are from Canada, diesel fuel GHG emissions sourced from tar-sand will be mitigated.
- Life-cycle study assumed 24.4 mpg.
- Tar sands produce 0.54 ton $CO_2$/bbl.
- F-T Fuel derived from coal produces 0.96 ton $CO_2$/bbl.



# Electrolysis Model: Inputs

- Cost/value of products and reactants
- Current efficiency of products (selectivity)
- Current density and cell potential
- Capital costs ($/kW electrical capacity, based on electrolysis analyses)
- Unit capacity
- Unit efficiency (based on 75% efficiency for electrolyzers based on HHV of H2)

# Electrolysis Model: Outputs

- Required catalyst area
- Rate of production/consumption of electricity and materials
- Costs and revenue
- Rate of energy production of products (based on HHV)
- Energy efficiency of electrical storage (based on HHV and overall unit input)
- Net profit
- Net capital cost
- Operating time for return of initial investment (if positive net profit)

# Running Condition (Electrolyzer)

- Capacity: 1 MW
- Investment: 825 M$
  - Capital cost: $600 M$
  - M & O cost: $225 M$ (labor, replacements)
- Capacity factor: 80 %
- Running 6 hours
- Lifetime : 40 years
  - Cell stacks should be replaced in 10 years

NREL *Summary of Electrolytic Hydrogen Production: Milestone Completion Report, 2004.*

# Running Condition (F-T)

- Capacity: 120 MW
- Investment: M$

  Capital cost: $19.6M$

  M & O cost: $5.88M$ (labor, replacements)
- Running 6 hours
- Lifetime : 40 years
- $CO_2$

  0.54 ton $CO_2$ / barrel of F-T liquid

  $3.78- $13 / bbl $CO_2$ Credit

NREL *Summary of Electrolytic Hydrogen Production: Milestone Completion Report, 2004.*

# F-T process

- $167,000 / MW
- Capacity: 120 MW
- 19.6 M$
- Conversion rate: 80 % (20 %: heat, off-gas)

- 0.54 ton $CO_2$ / barrel of F-T liquid
- $3.78- $13 / bbl $CO_2$ Credit

# Input & output

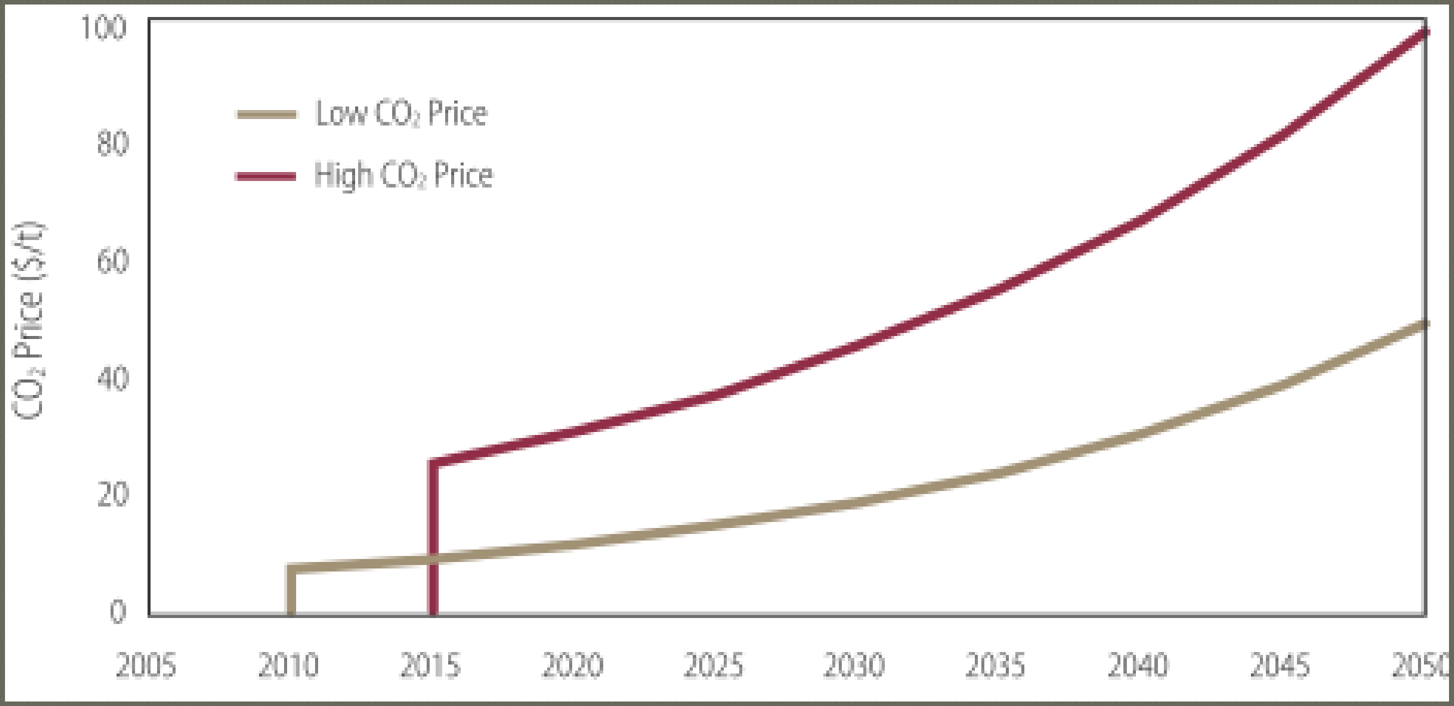
Inputs

- $CO_2$: free
- Industrial water: $7.424*10^{-4}$ \$/kg
- Electricity: 0.05 \$/kWh (Wind, LCOE by EERE)

Outputs

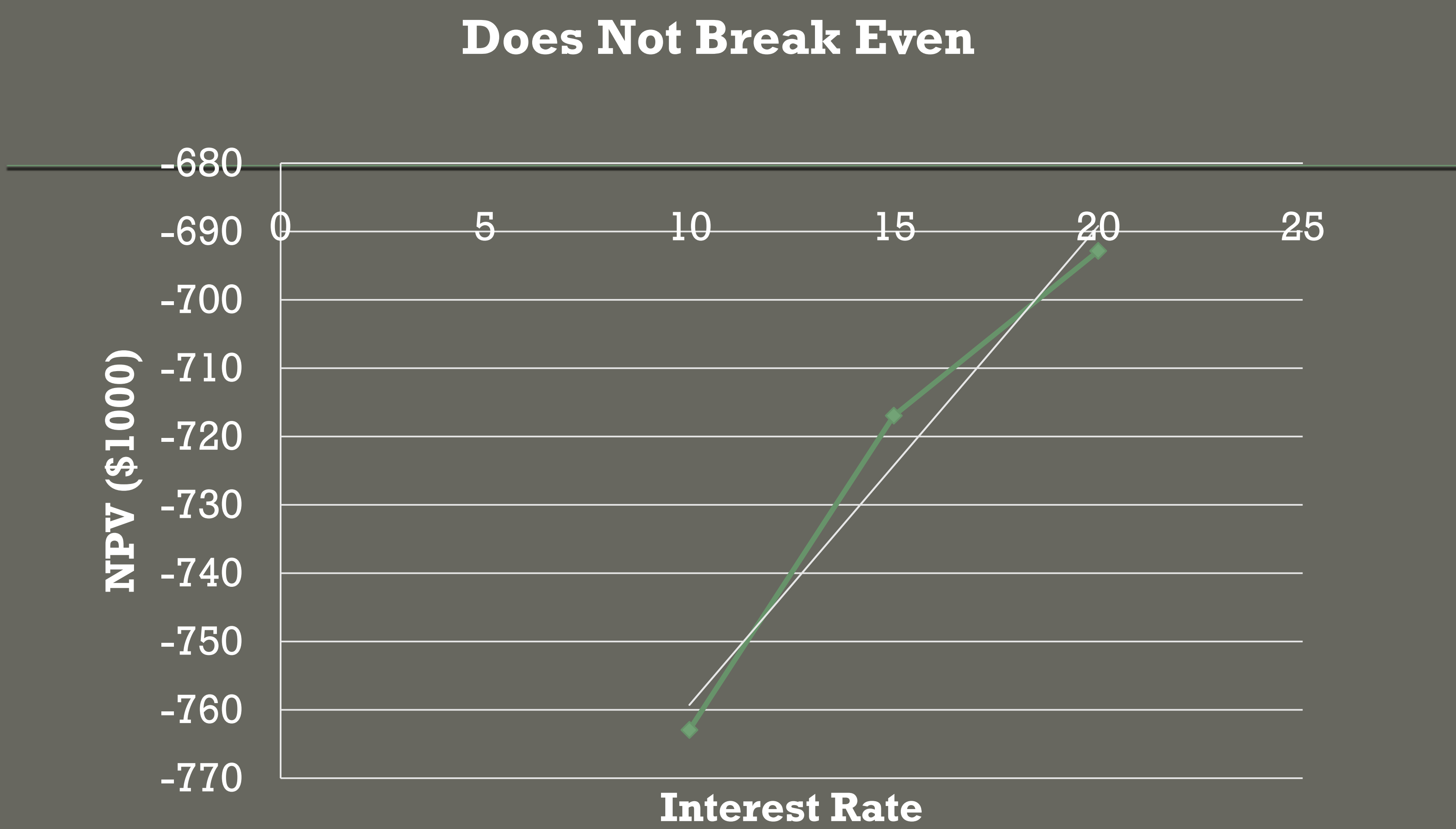
- Diesel 0.96 \$/kg
- Gasoline 1.03 \$/kg
- Kerosene 1.01 \$/kg

# Additional factor 1: Carbon taxes




Low: CCS plays a key role. Prefable, begin with 5 $/mt
High: CCS plays a key role. Cap-and-trade works well under Kyoto-protocol,
begin with 25 $/mt

The Future of Coal, Massachusetts Institute of Technology: 2007. http://web.mit.edu/coal/The_Future_of_Coal.pdf.



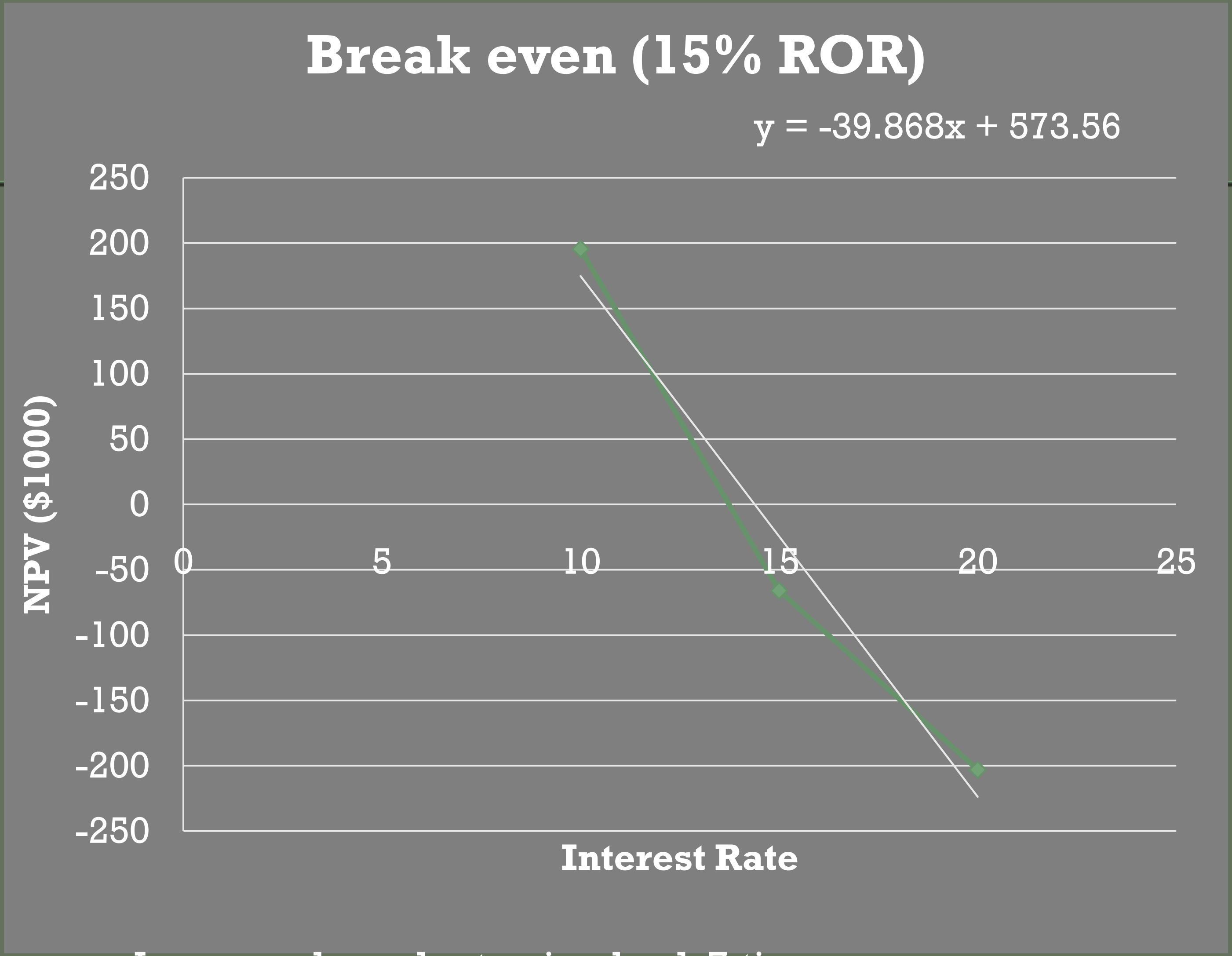

Too far from break even…

Varying factors:

Products price

Capital cost

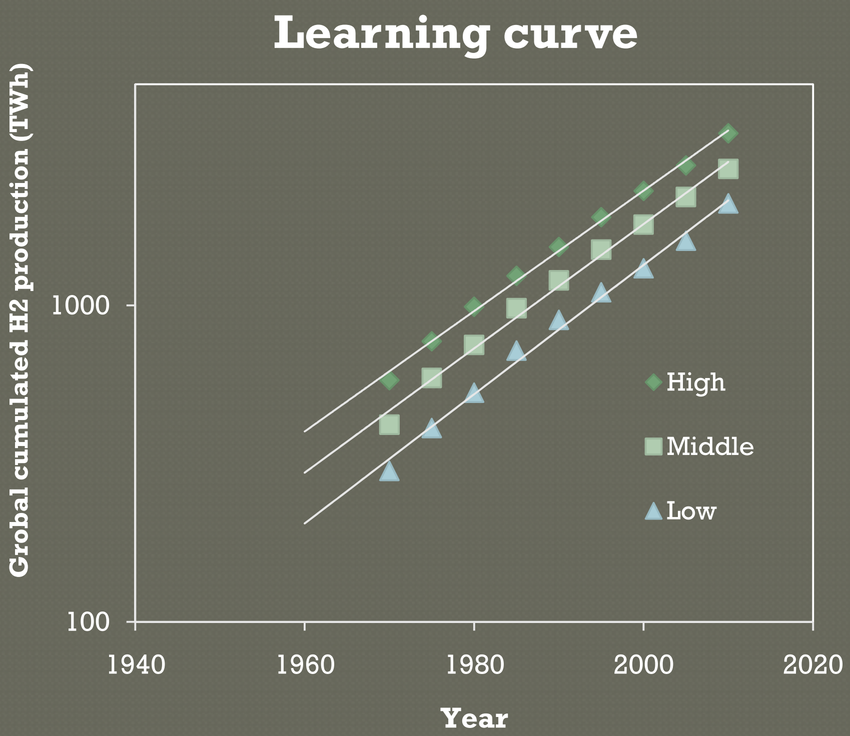
Electricity cost



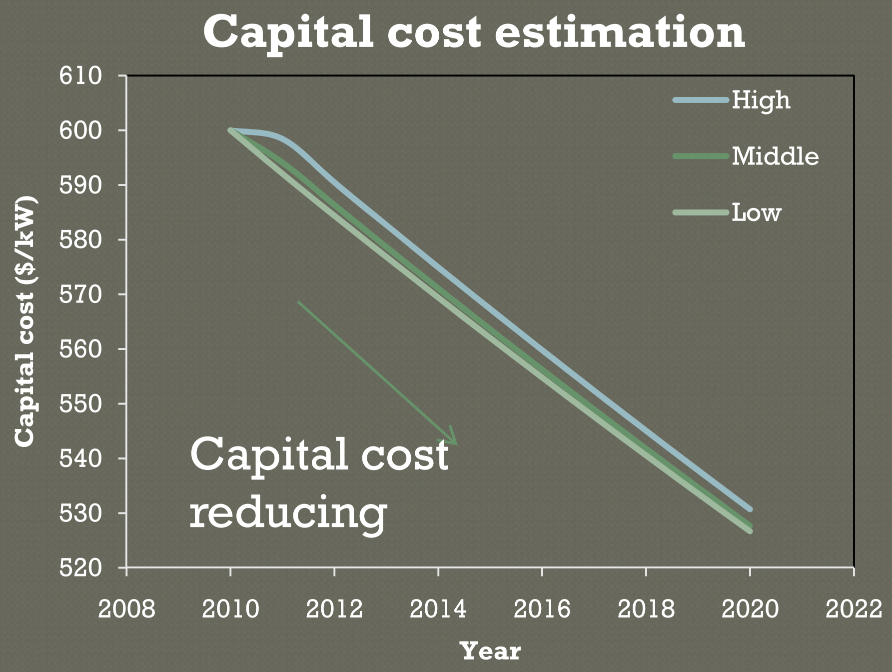

Increased product price by 1.7 times.
(14 years, 20 % of rate of return)

# Capital cost

- Learning curve estimation $c_t = c_0 (n_t / n_0)^{\alpha}$

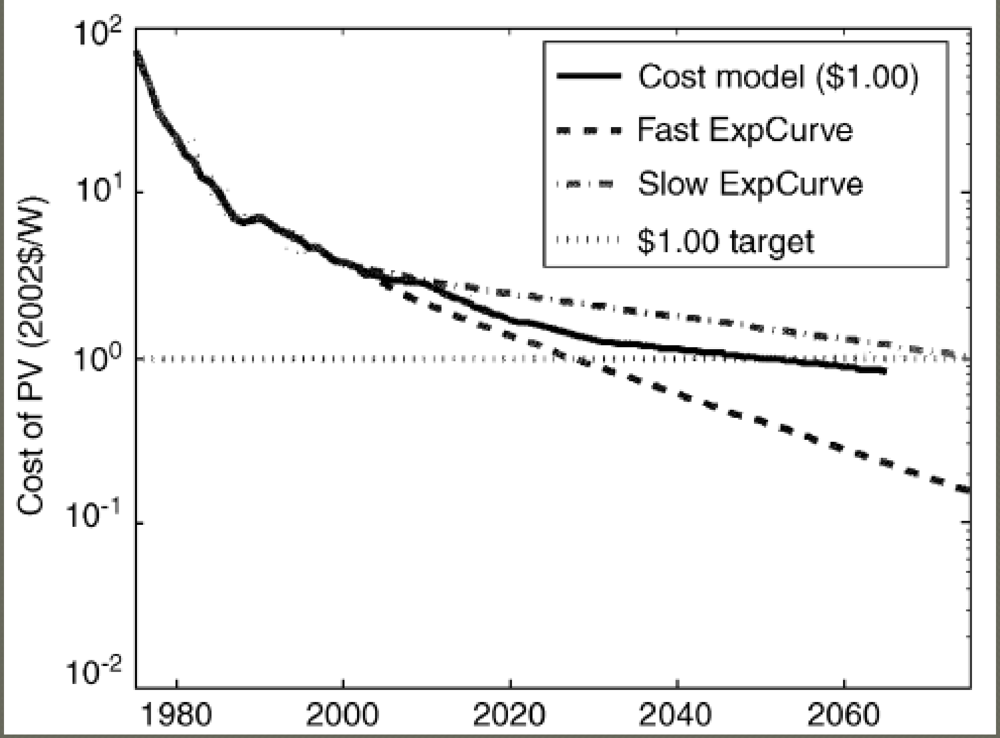



Learning rate = 80%



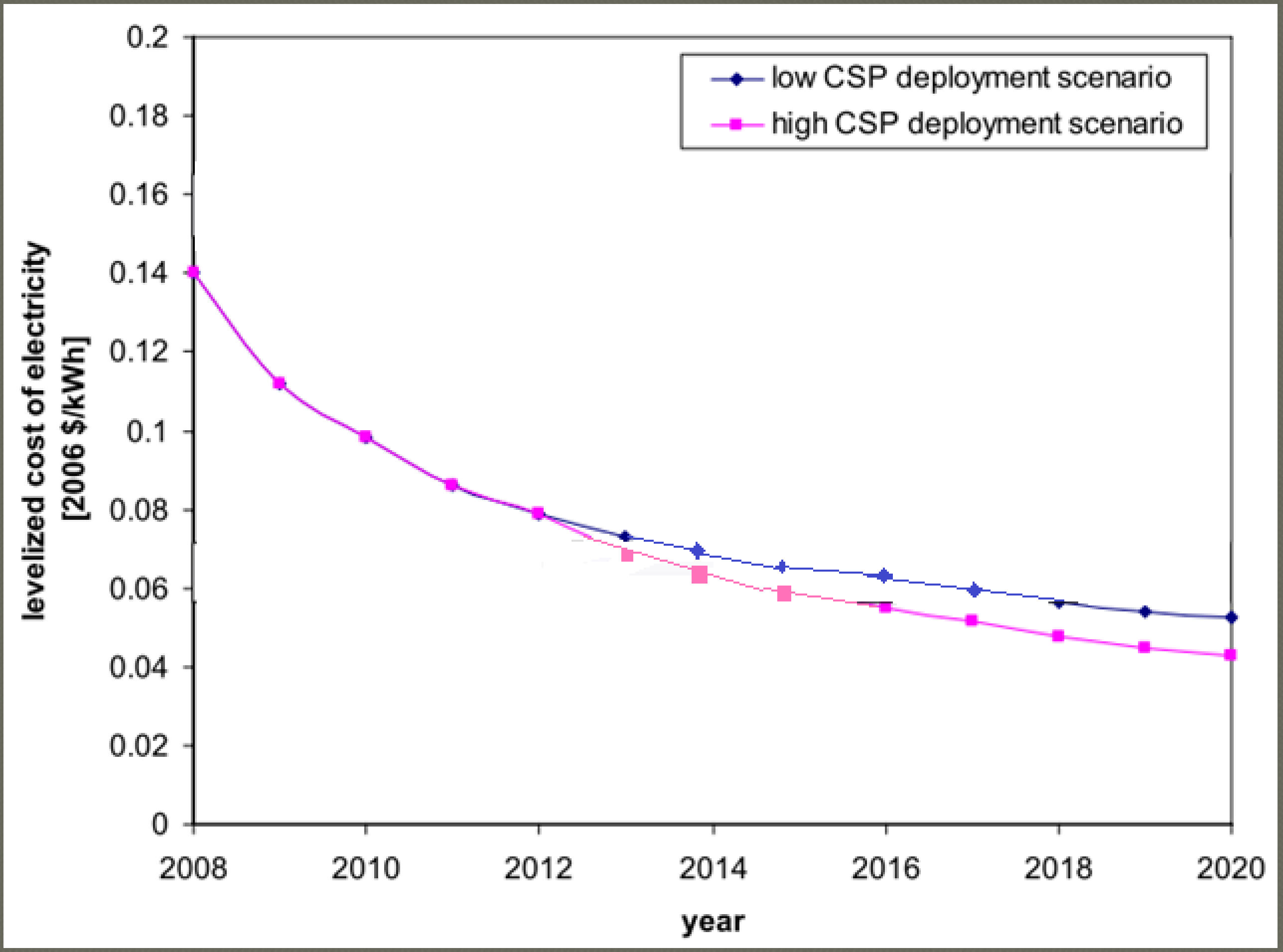

Schoots, K.; Ferioli, F.; Kramer, G. J.; van der Zwaan, B. C. C. *International Journal of Hydrogen Energy* ***2008, 33, 2630-2645.***

# Electricity Cost -PV



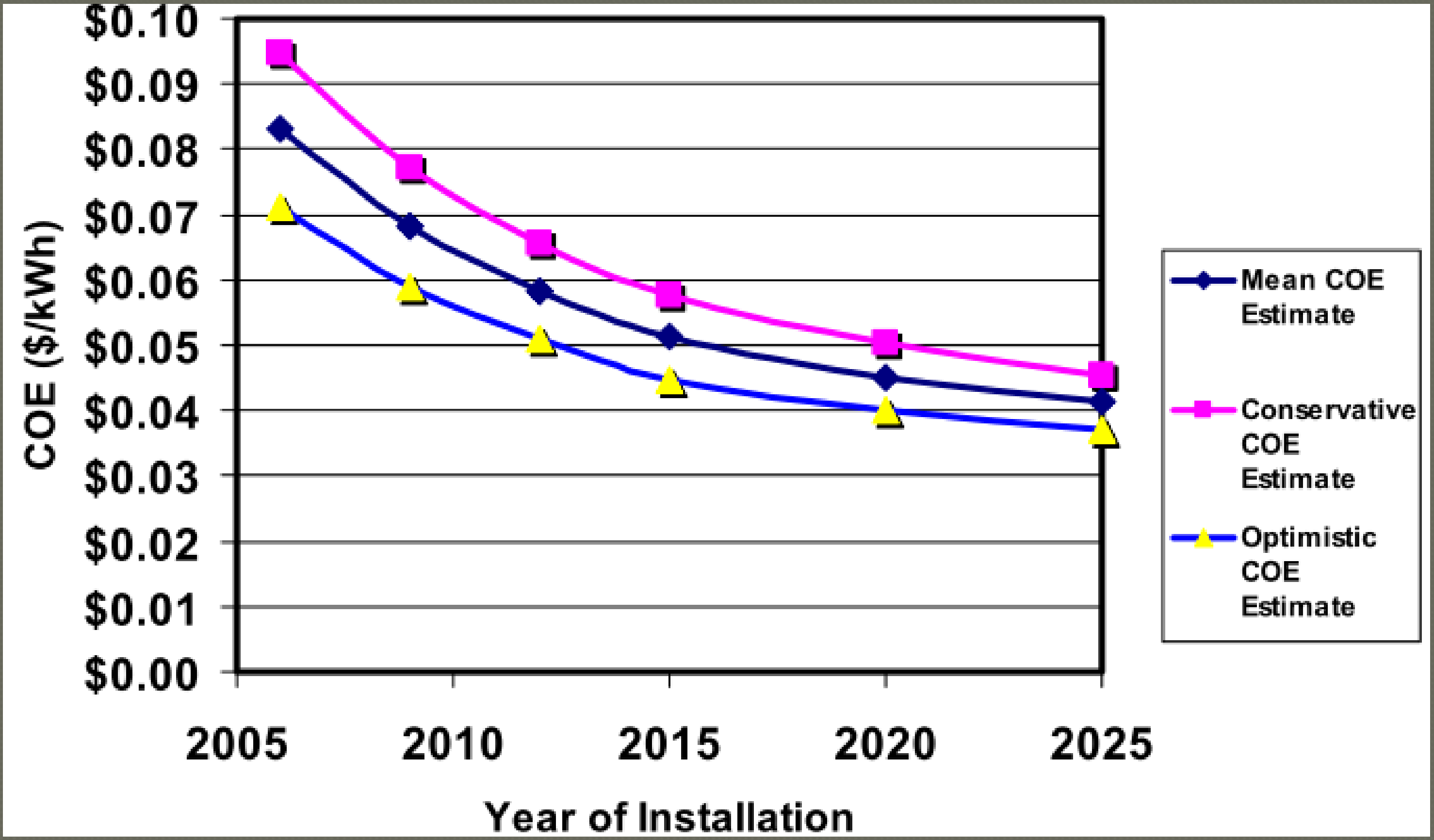

Nemet, G. F., Beyond the learning curve: factors influencing cost reductions in photovoltaics. *Energy Policy* ***2006, 34, (17), 3218-3232.***

# Electricity Cost - CSP




Zimmer, V.L., Woo, C., & Schwartz, P., Concentrated Solar Power for Santa Barbara County: Analysis of High Efficiency Photovoltaic and Thermal Solar Electric, ERG 226, December 2006.

# Electricity Cost - Wind




NREL *Future for Offshore wind power Energy in the United States, 2004.*

# Areas for Improvement

- Reduce electricity costs by reducing cell potential
- Could increase selectivity
- Must greatly increase current density

# Conclusions

- Electricity is the major operating cost
  - Water is negligible, CO2 generally 10% or less
- While our process mitigates significant $CO_2$ emissions, there are no economic incentives or benefits for doing so.
- Methanol and F-T diesel could be done
  - Methane is just too inexpensive and inefficient.
- Higher value and efficiency of hydrogen generation shows greater promise(to some products?)

# Conclusions

- Could find use for specialty petroleum derived chemicals
  - Ethylene, formic acid
- Not economically feasible at current conditions.
  - If diesel and gasoline reach higher prices, ~ \$5/gal, process becomes economical.
  - Carbon-taxes would help significantly.

# Critical analysis

- Capital, operating, and energy costs not included
  - This would make results less feasible
- Storage, transportation, and handling costs not considered
- Large scale use would require a massive renewable energy infrastructure to be carbon neutral
- Considerable carbon taxes/credits would need to be implemented