Sunshine to Petrol

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Technoeconomics for Sunshine to Petrol:
Approach, Results, Challenges and Lessons Learned

Presented by:

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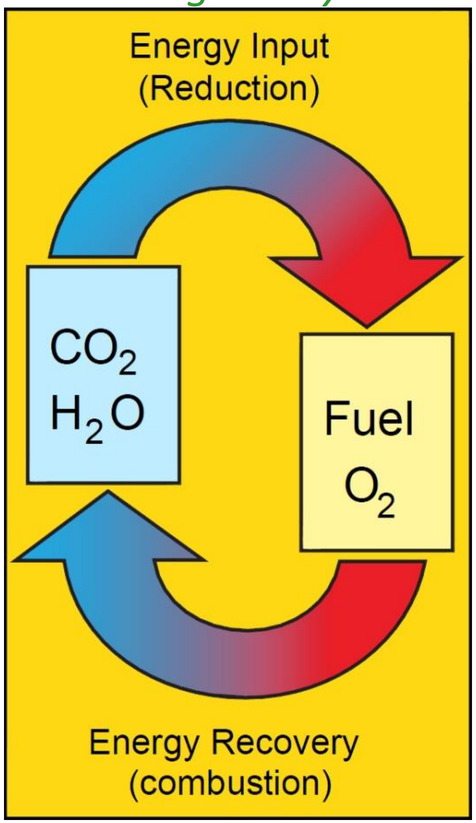
2013

Sunshine to Petrol

Closing the Cycle



For now and for transportation fuels, liquid hydrocarbons are the "Gold Standard"

Vision: Directly apply a solar thermal energy source to effectively reverse combustion and "energize" CO_2 and H_2O into hydrocarbon form in a process analogous to the one that produces bio- and fossil fuels but at higher solar to fuel efficiency.

$$\text{Sunlight} + CO_2 + H_2O \rightarrow \text{Fuel} + O_2$$

Big Picture: A Question of Impact

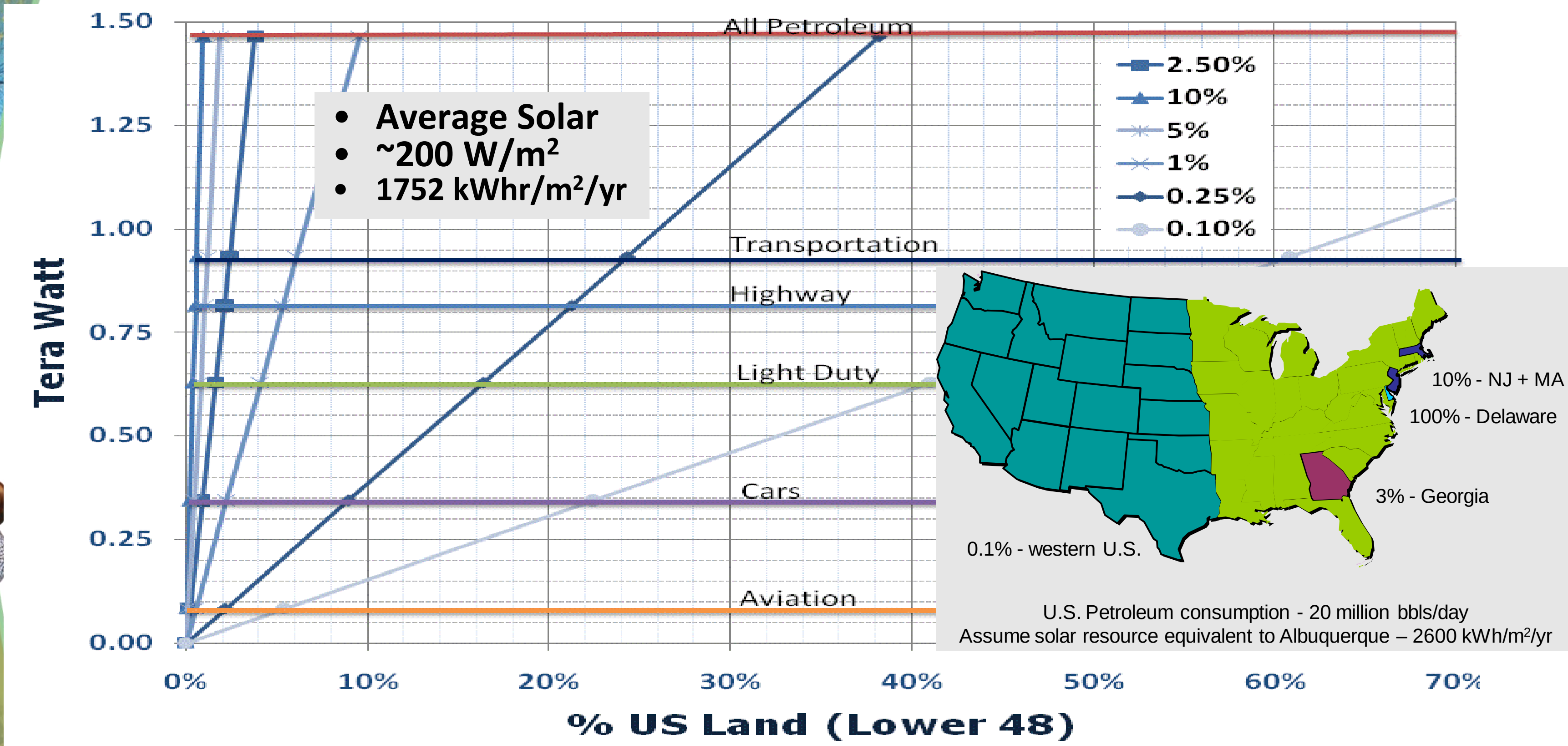
- If we are wildly successful, does it matter?
- What are limits and limiting factors?
- Can we draw conclusions, set targets, etc.?
- Factors to consider
  - Problem definition – what is the scale?
  - Resources: CO_2, H_2O, Solar, Land, Materials
  - Economics
  - Timeframe

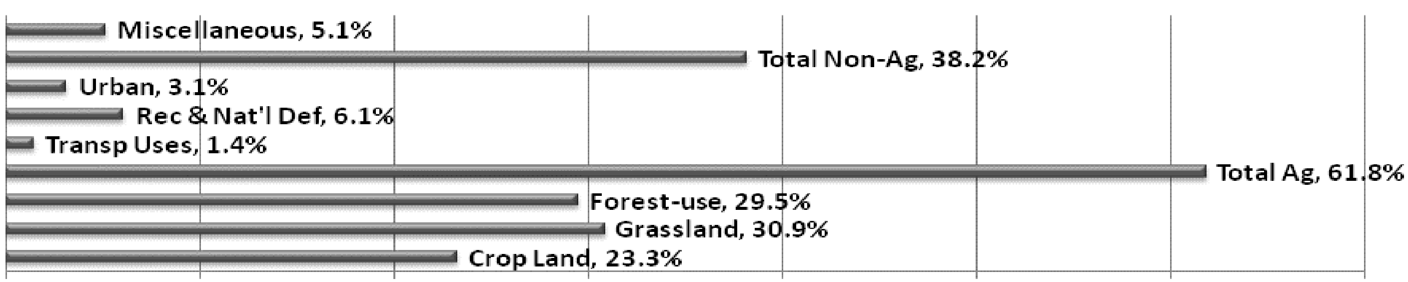
Meeting 100% of transportation demand with solar fuel is plausible

- High solar to fuel efficiency (>10%) is absolutely required.
  - Cost
  - Scale (land, materials of construction)
- Water, CO_2 are not limiting –
  - Water consumption/cost relatively low
  - High impact opportunity for CO_2.
- Consistent with other human activities occurring over multiple decades.

Ellen B. Stechel and James E. Miller "Re-energizing CO_2 to fuels with the sun: Issues of efficiency, scale, and economics" in press J. CO_2 Util. (2013), http://dx.doi.org/10.1016/j.jcou.2013.03.008.

Efficiency defines collector area



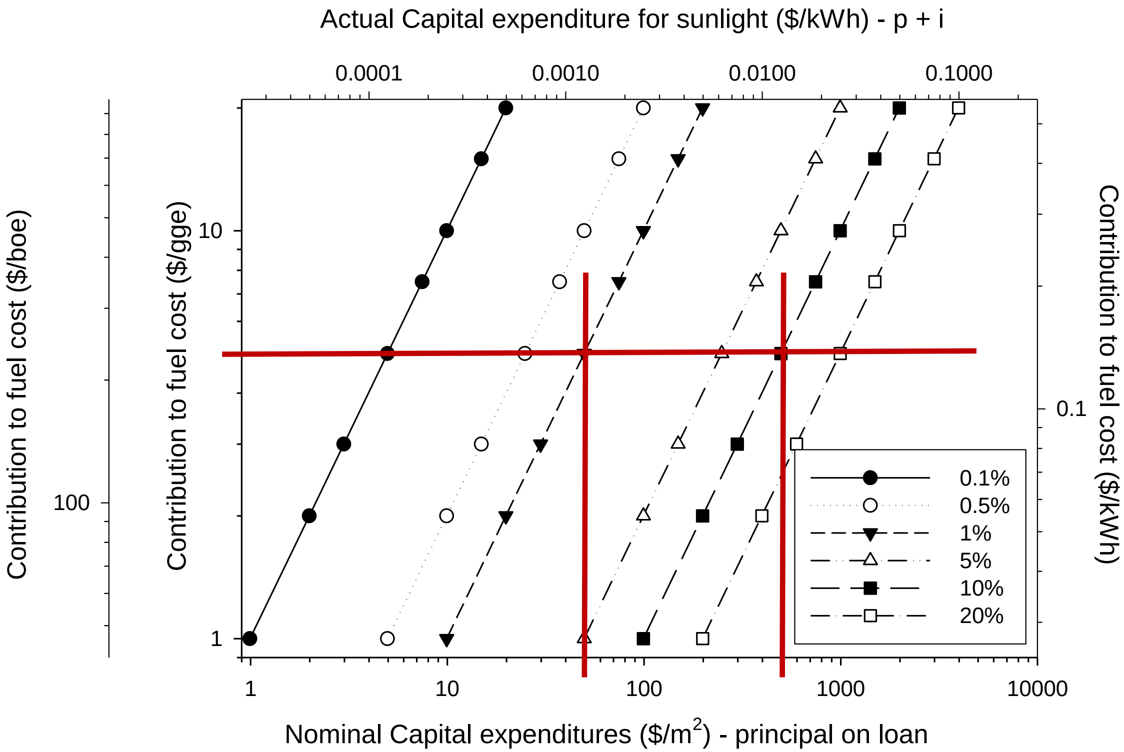


Efficiency drives Costs

For capital cost < $5/gge, expenditure can be no more than:

$50/m^2 for 1% Eff. (solar to fuel)

$500/m^2 for 10% Eff. (solar to fuel)



Benchmarks:

$1/m^2 ≈ $4,000/acre

6" Concrete slab ≈ $20/m^2

PE Greenhouse ≈ $80/m^2

Parabolic dish ~ $300/m^2

E.B. Stechel and J.E. Miller "Re-energizing CO_2 to fuels with the sun: Issues of efficiency, scale, and economics" Journal of CO2 Utilization http://dx.doi.org/10.1016/j.jcou.2013.03.008.

Assumptions: gge = 36 kWh, solar resource = 2365 kWh/m^2/yr, favorable financing (5% interest, 30 years)

There is such a thing as too low an efficiency, even for "inexpensive materials"

The Technology

Capitalize on decades of Synfuel technology, e.g.

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$

Build on these two reactions:

$4H_2O$ + energy $\rightarrow 4H_2 + 2O_2$ (water splitting)

$2CO_2$ + energy $\rightarrow 2CO + O_2$ (carbon dioxide splitting)

$2CO_2 + 4H_2O$ + energy $\rightarrow 2CO + 4H_2 + 3O_2$

WS and CDS are linked by the Water Gas Shift reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Only necessary to conduct one of the two to accomplish the chemistry

Establish Metrics – Current Technology

Technology	Solar to electricity[b]	Electricity to hydrogen[c]	Solar to hydrogen
Photovoltaic/AE[a]	15%	73%	11%
Molten Salt Tower/AE	18%	73%	13%
Dish Stirling/AE	24%	73%	18%

[a]Alkaline electrolysis

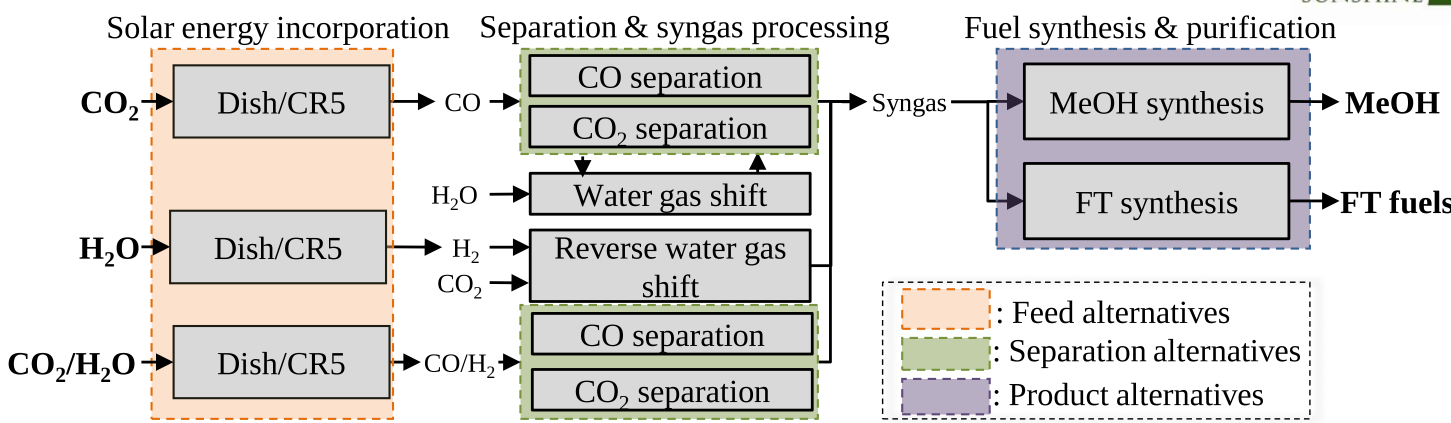
[b]These are estimated annual average efficiency values

[c]This performance value is at the high end for an alkaline electrolyzer, is dependent on system operation as well as size, and is based on the higher heating value (HHV) of the hydrogen product.

Literature and out own early work suggests 40-50% H_2 to Fuel possible

(1) *Electrical to Fuel; Mignard and Pritchard Trans IChemE, Part A, September 2006.*
(2) *H_2 + utilities to Methanol; Henao, Maravelias, Miller and Kemp, presented @ FOCAPD 2009.*

Multiple Pathways Considered Assume - 20% Solar to CO/H_2



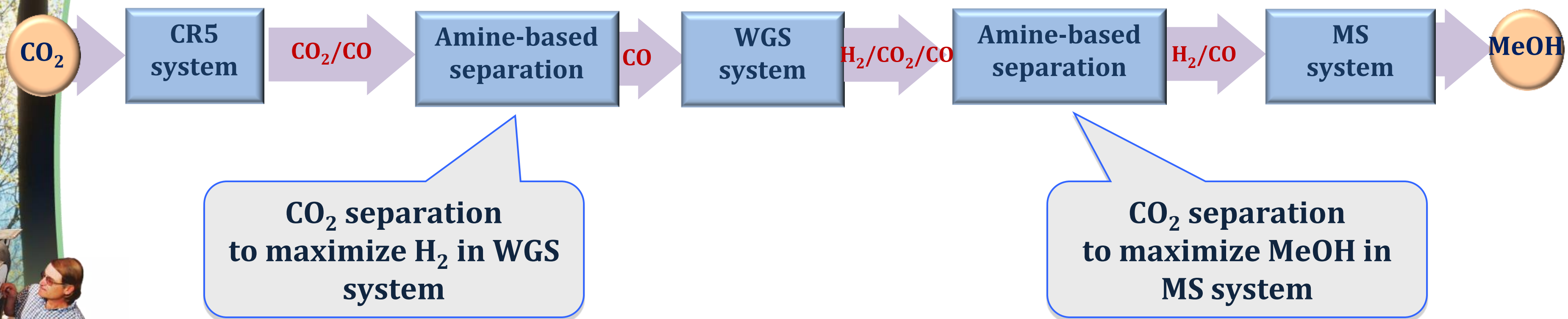
	Pathway	Energizing Reaction	CO_2/CO separation	Fuel
A	CO_2	CO_2	CO_2	MeOH
B	H_2O	H_2O	-	MeOH
C	Mixed	CO_2 / H_2O	CO_2	MeOH
D	Mixed FT	CO_2 / H_2O	CO_2	FT fuels
E	CO_2 –CO Sep.	CO_2	CO	MeOH
F	Mixed CO Sep.	CO_2 / H_2O	CO	MeOH

University of Wisconsin – Dr. Christos Maravelias' group/ / Sandia

Process Synthesis

CO_2 pathway for MeOH production

Basic configuration



Slides 9-27:
Jiyong Kim, Carlos A. Henao, Terry A. Johnson, Daniel E. Dedrick, James E. Miller, Ellen B. Stechel and Christos T. Maravelias "Methanol production from CO_2 using solar-thermal energy: process development and techno-economic analysis" Energy Environ. Sci., 2011, 4, 3122.

Jiyong Kim, Terry A. Johnson, James E. Miller, Ellen B. Stechel and Christos T. Maravelias "Fuel production from CO_2 using solar-thermal energy: system level analysis" Energy Environ. Sci., 2012, 5, 8417.

Process Synthesis

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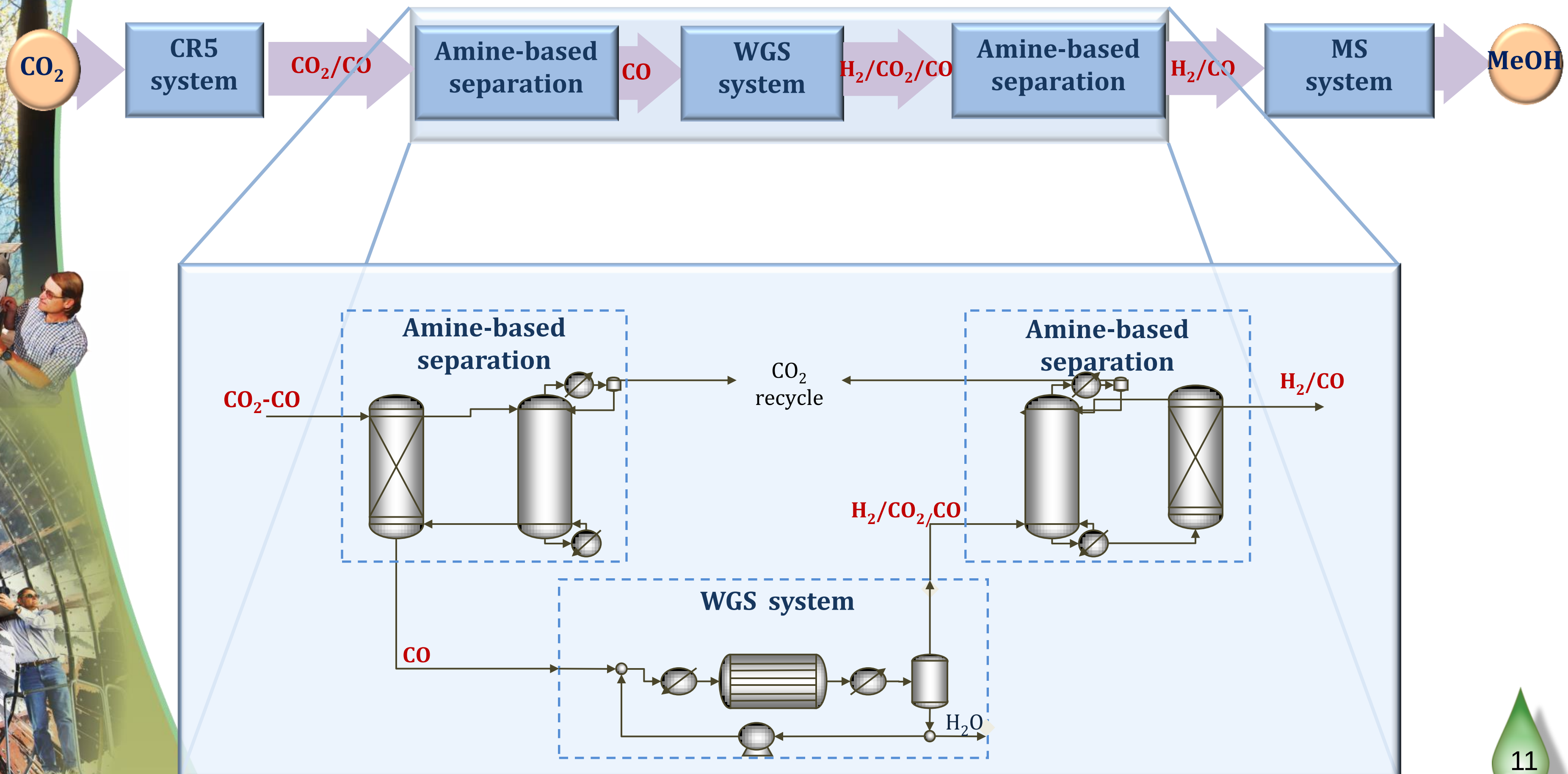
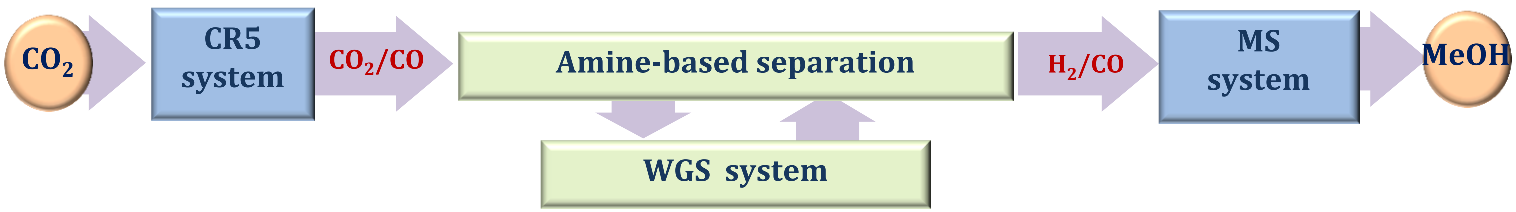


All units (regenerator, heat exchanger and pump) are duplicated.

Process Synthesis

CO_2 pathway for MeOH production

Improved amine-based separation network



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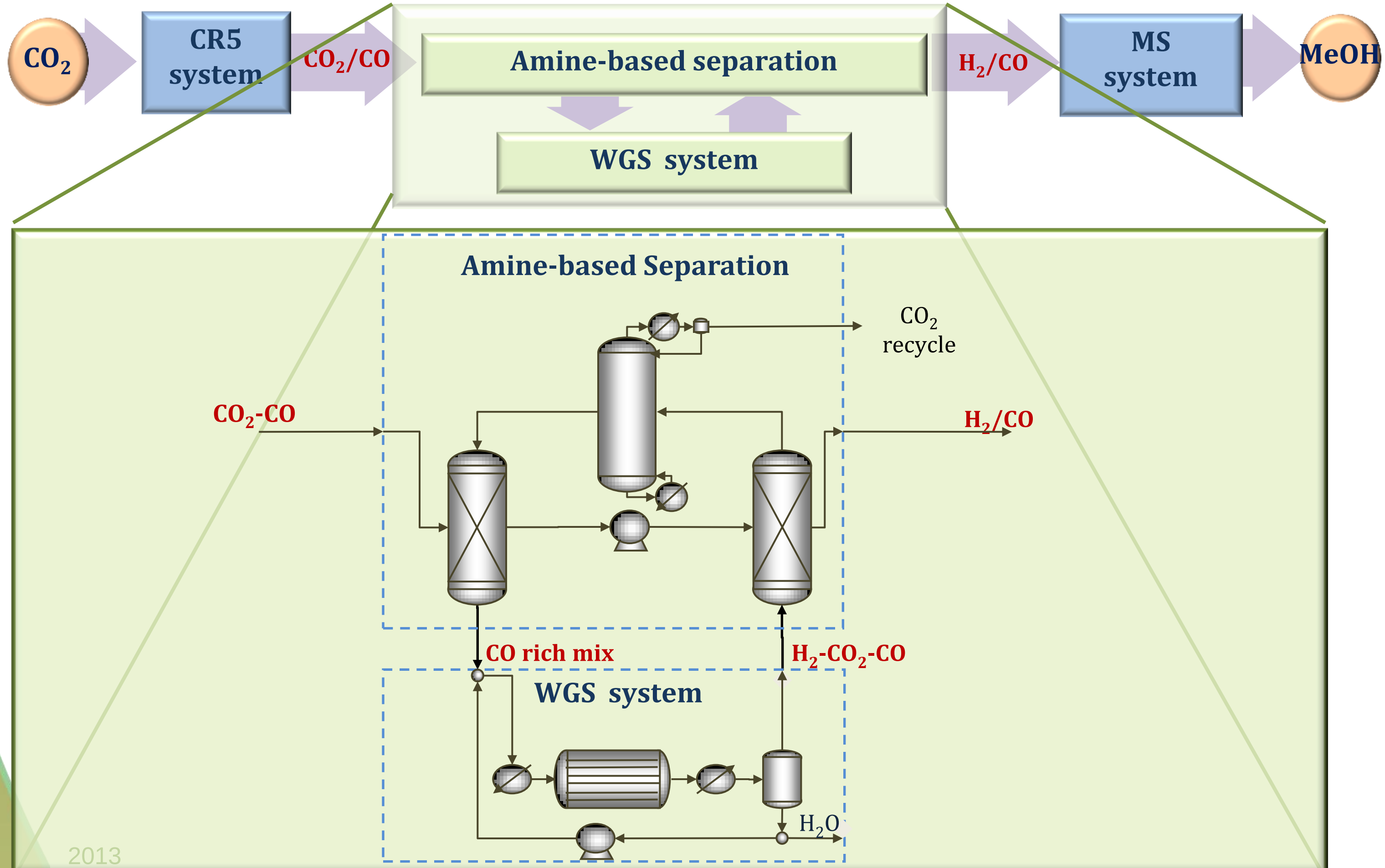
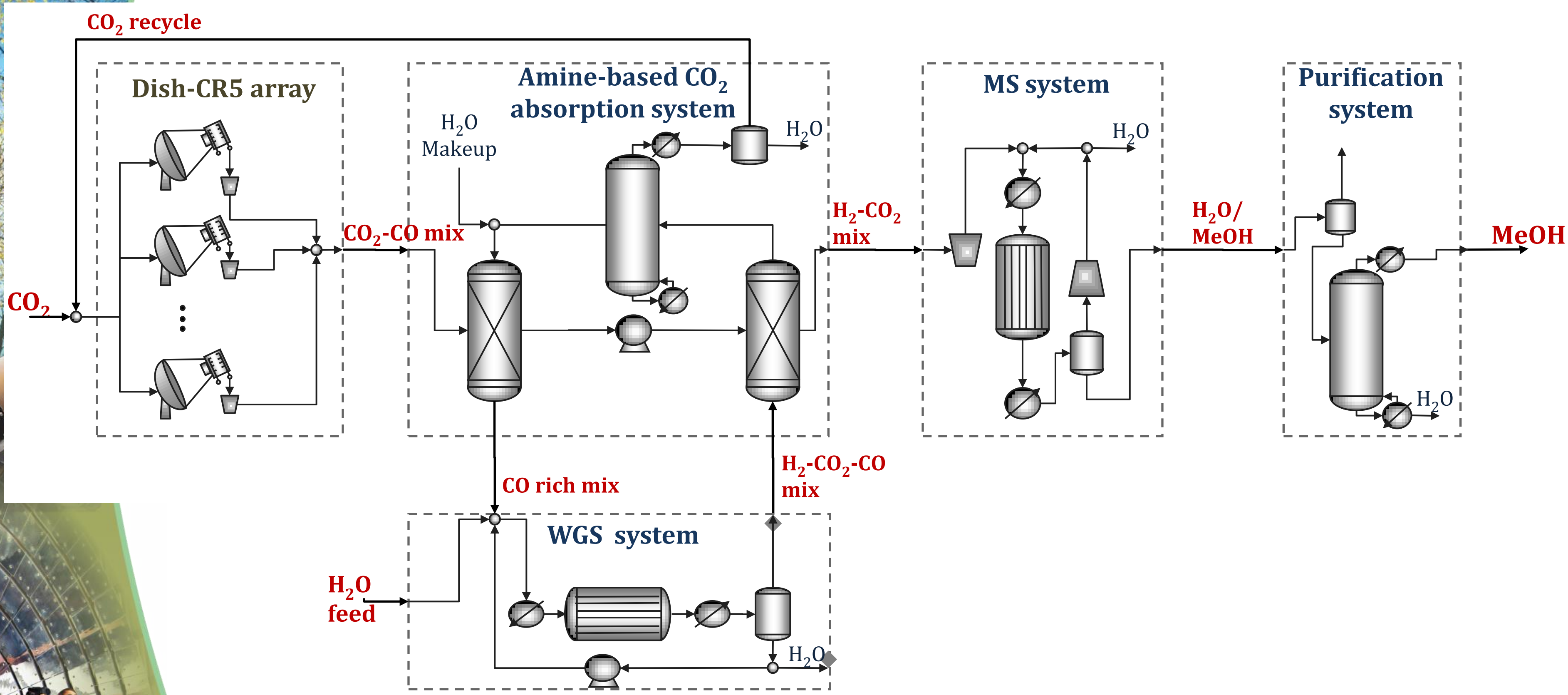


Process Simulation

Process flow diagram (PFD) of CO_2 pathway for MeOH production



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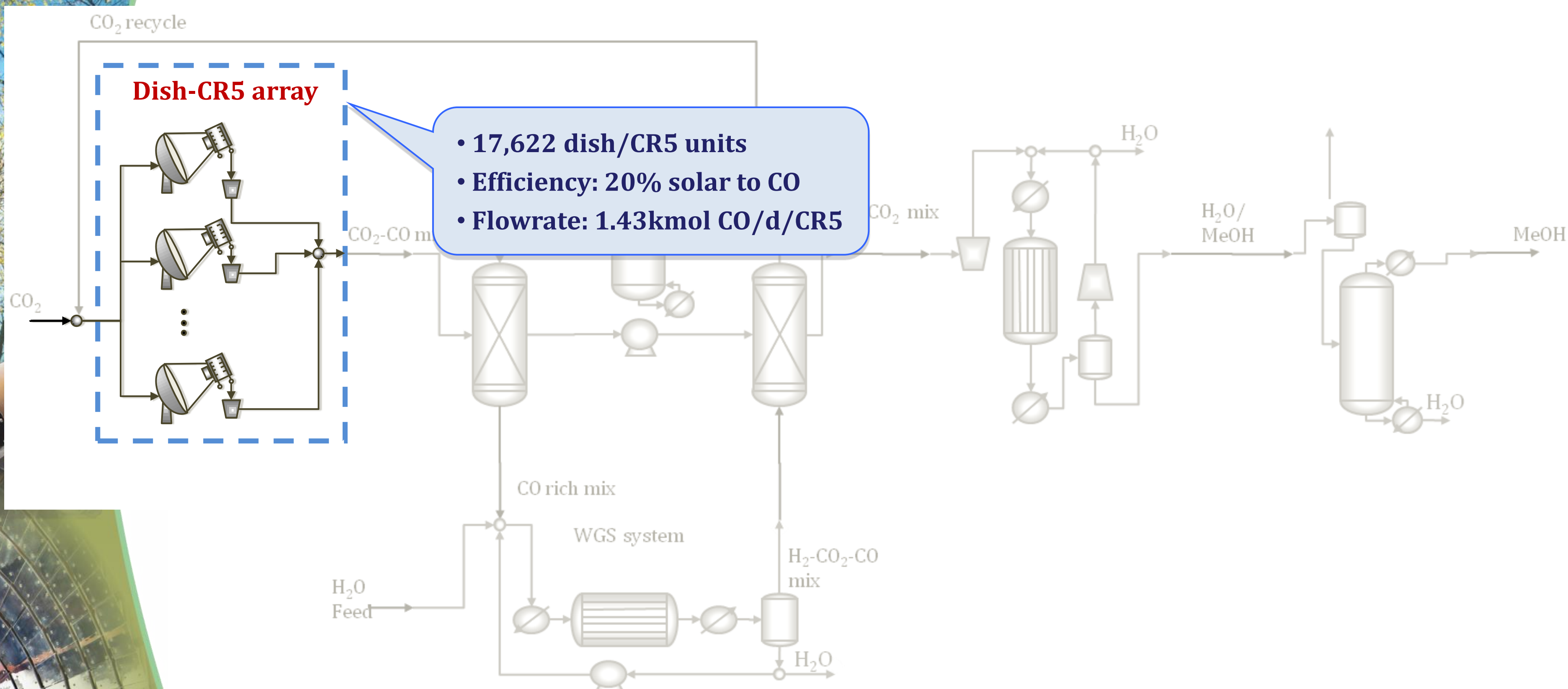
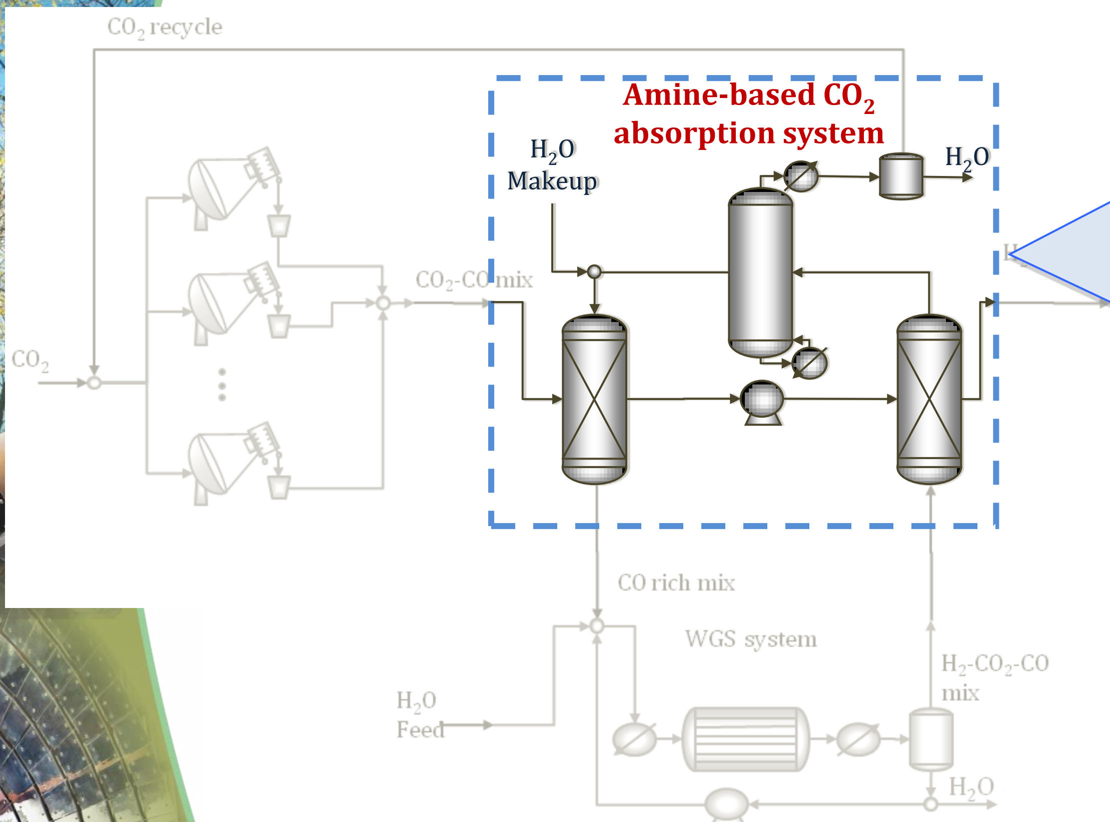


- 17,622 dish/CR5 units
- Efficiency: 20% solar to CO
- Flowrate: 1.43kmol CO/d/CR5

Process Simulation

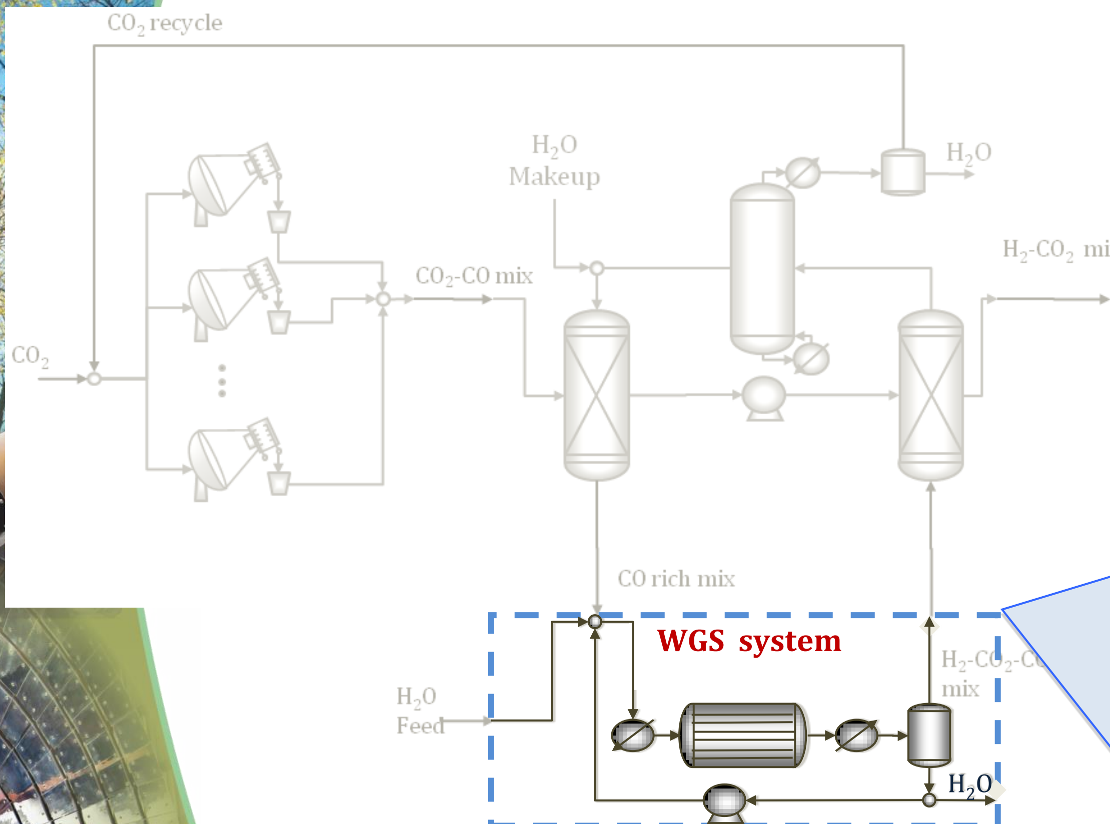
Process flow diagram (PFD) of CO_2 pathway for MeOH production



- MEA concentration: 25 wt%
- Operating conditions
  - 1st Absorber: 42°C , 1.1 atm
  - 2nd Absorber: 46°C, 20 atm
  - Regenerator: 42~72°C, 1.2 atm
    - Reboiler duty: 5,111 kW
    - Condenser duty: -4,901 kW
- Optimized variables: T, P, CO_2 loading

Process Simulation

Process flow diagram (PFD) of CO_2 pathway for MeOH production



- **WGS reactor:**

  $CO + H_2O \leftrightarrow CO_2 + H_2$
- **Catalyst : $Cu/ZnO/Al_2O_3$**
- **Kinetics**

$$r_{WGS} = \frac{k_4 \cdot P_{CO_2} \cdot \left(1 - \frac{1}{K_{WGS}} \cdot \frac{P_{H_2O} \cdot P_{CO}}{P_{H_2}{}^{3} \cdot P_{CO_2}}\right)}{\left(1 + k_3 \cdot \frac{P_{H_2O}}{P_{H_2}} + k_1 \cdot \sqrt{P_{H_2}} + k_2 \cdot P_{H_2O}\right)}$$

$$k_1 = 0.499 \cdot e^{\frac{17197}{R \cdot T}}, k_2 = 6.62E-11 \cdot e^{\frac{124119}{R \cdot T}},$$

$$k_3 = 3453.38, k_4 = 1.22E10 \cdot e^{\frac{-94765}{R \cdot T}}, K_{WGS} = 10^{\left[\frac{-2073}{T} + 2.029\right]}$$

- **Feed ratio: $CO/CO_2/H_2$ = 0.34/0.05/0.61**
- **Reactor inlet condition: 280°C , 21.2 atm**
- **Optimized variables: T, P , feed ratio.**

Process Simulation

Process flow diagram (PFD) of CO_2 pathway for MeOH production

- **MS reactor:**

$$CO + 2H_2 \rightarrow CH_3OH$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

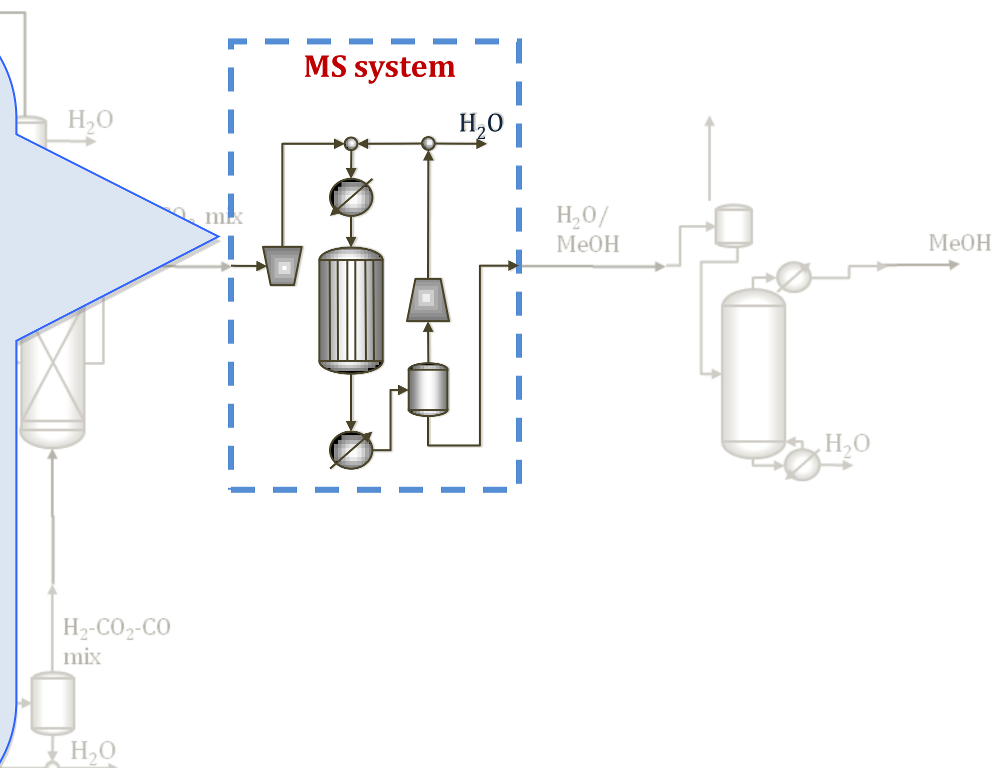
- **Catalyst : $Cu/ZnO/Al_2O_3$**
- **Kinetics**

$$r_{MS} = \frac{k_3 \cdot P_{CO_2} \cdot P_{H_2} \cdot \left(1 - \frac{1}{K_{MS}} \cdot \frac{P_{H_2O} \cdot P_{CH_3OH}}{P_{H_2}{}^3 \cdot P_{CO_2}}\right)}{\left(1 + k_3 \cdot \frac{P_{H_2O}}{P_{H_2}} + k_1 \cdot \sqrt{P_{H_2}} + k_2 \cdot P_{H_2O}\right)^3}$$

$$k_1 = 0.499 \cdot e^{\frac{17197}{R \cdot T}}, k_2 = 6.62E - 11 \cdot e^{\frac{124119}{R \cdot T}}$$

$$k_3 = 1.07 \cdot e^{\frac{36696}{R \cdot T}}, K_{MS} = 10^{\left[\frac{3066}{T} - 10.592\right]}$$

- **Reactor inlet condition: 210°C , 46.2 atm**
- **Variables (T, P and feed composition) were adjusted to maximize MeOH.**



Process Simulation

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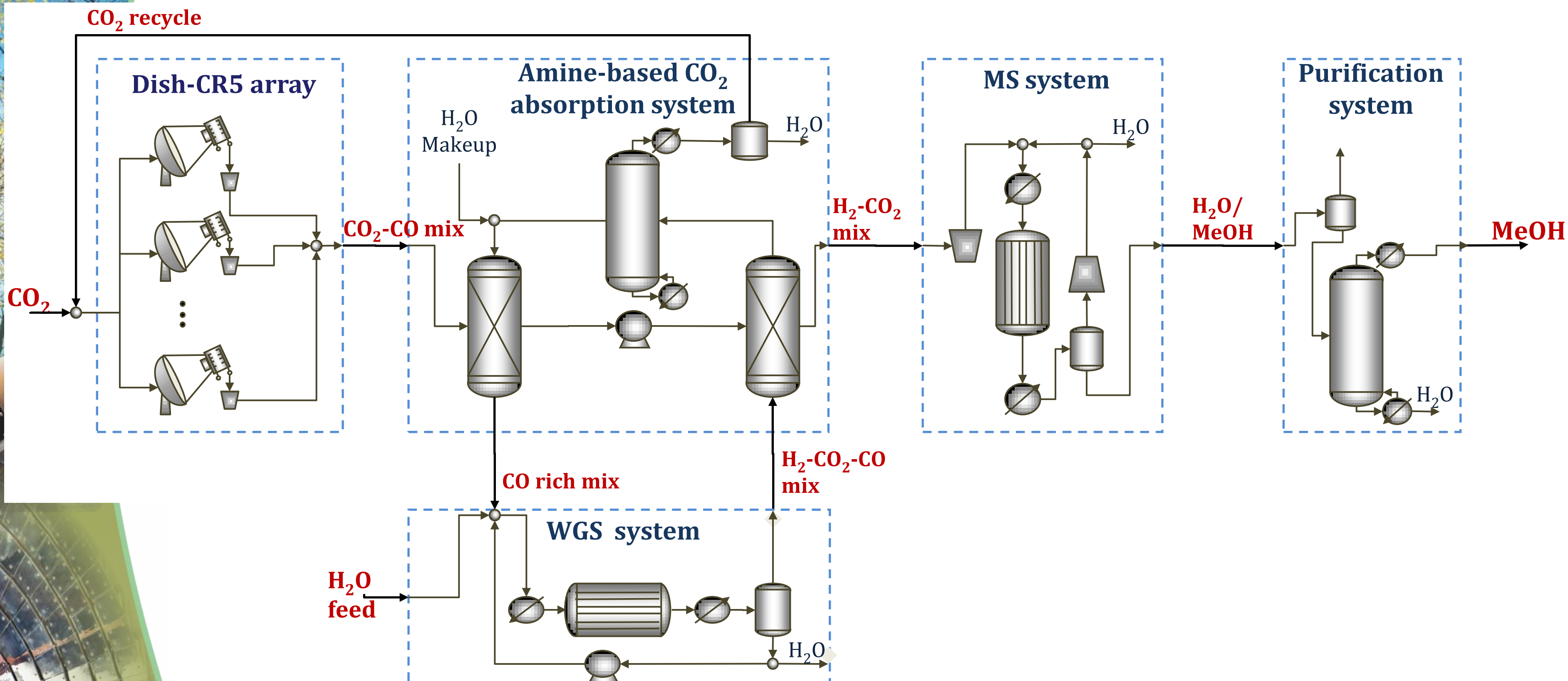
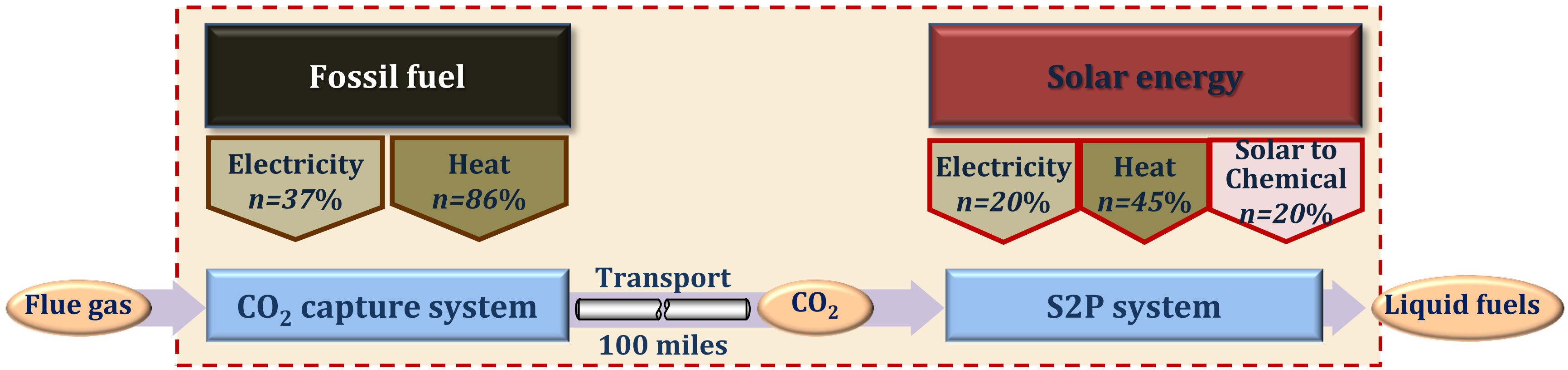


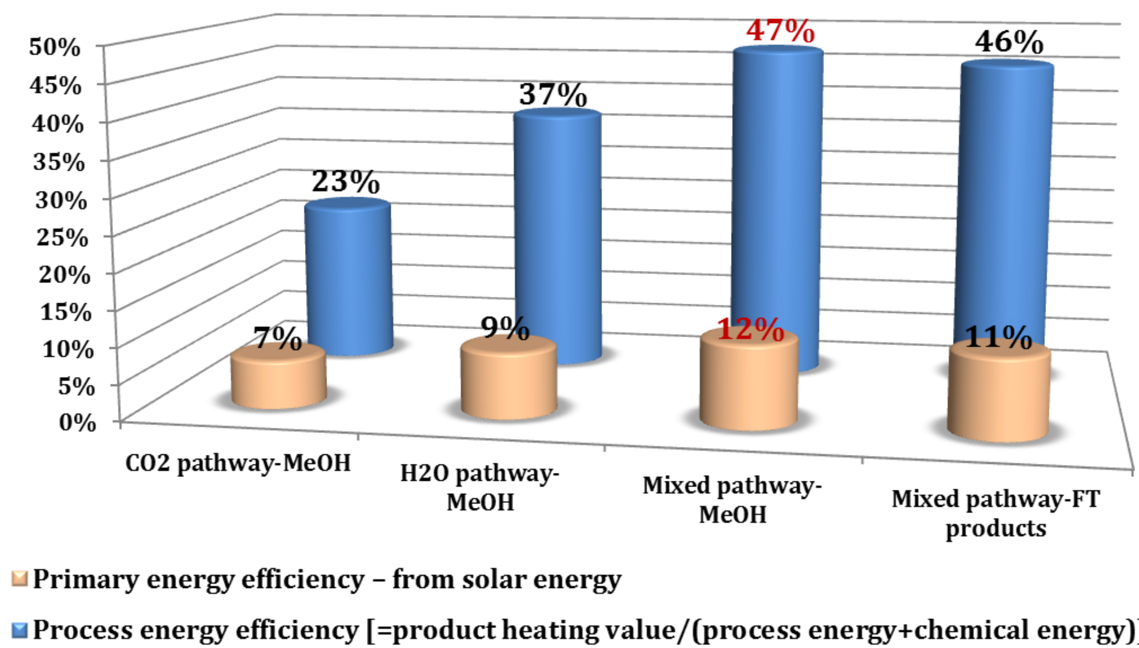
Mole flow (kmol/hr)	CO_2	CO_2-CO mix	CO rich mix	H_2O feed	H_2-CO_2-CO mix	H_2-CO_2 mix	H_2O/MeOH	MeOH
CO_2	431	3,246	1,055	-	790	48	54	-
CO	-	1,055	122	-	380	380	38	-
H_2	-	-	-	-	675	674	-	-
H_2O	-	-	15	673	-	-	338	1
MeOH	-	-	-	-	-	-	336	319

Sunshine to Petrol

Energy Efficiency

Primary energy efficiency- from solar energy





Economic Evaluation

Process simulation results: flows, T, P, heat duties

Sizing & costing data

Total capital investment (TCI) = **Direct plant cost** + **Indirect plant cost**

Direct plant cost:
- ✓Equipment cost
- ✓Equipment setting
- ✓Piping
- ✓Civil work
- ✓Steel & instrumentation
- ✓Electrical systems

Indirect plant cost:
- ✓Engineering & supervision
- ✓G&A and Overheads
- ✓Contract Fee
- ✓Contingencies

Economic Evaluation

Process simulation results: flows, T, P, heat duties

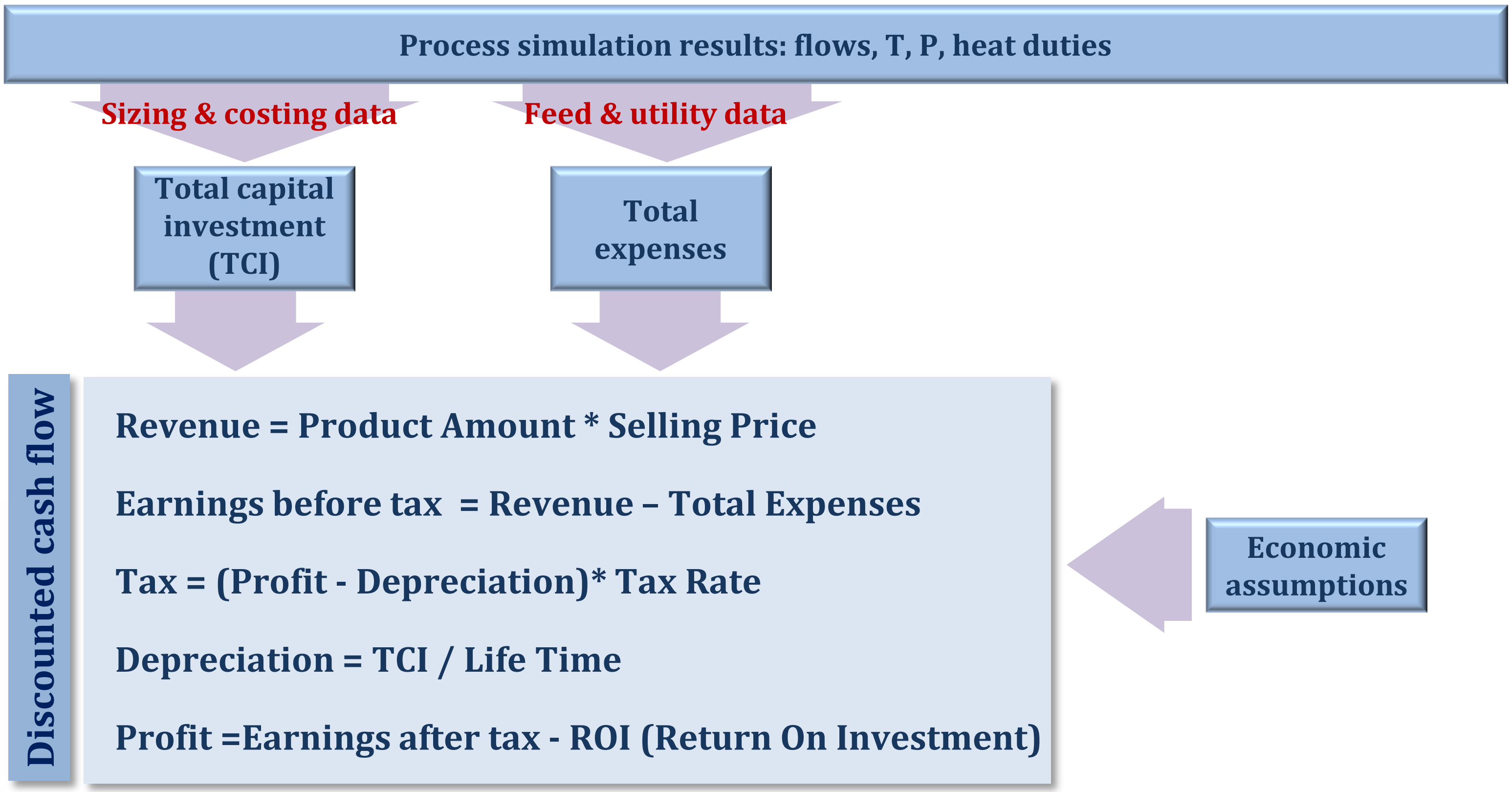
Sizing & costing data → **Total capital investment (TCI)**

Feed & utility data → **Total expenses** = **Variable expense** + **Fixed expense**

Variable expense:
- ✓ Utility
- ✓ Raw material

Fixed expense:
- ✓ Operating labor
- ✓ Supervision labor
- ✓ Operating supplies
- ✓ Maintenance

Economic Evaluation



Sunshine to Petrol

Economic Evaluation

Process simulation results: flows, T, P, heat duties

Sizing & costing data → Total capital investment (TCI)

Feed & utility data → Total expenses

Discounted cash flow

Revenue = Product Amount * Selling Price

Earnings before tax = Revenue – Total Expenses

Tax = (Profit - Depreciation)* Tax Rate

Depreciation = TCI / Life Time

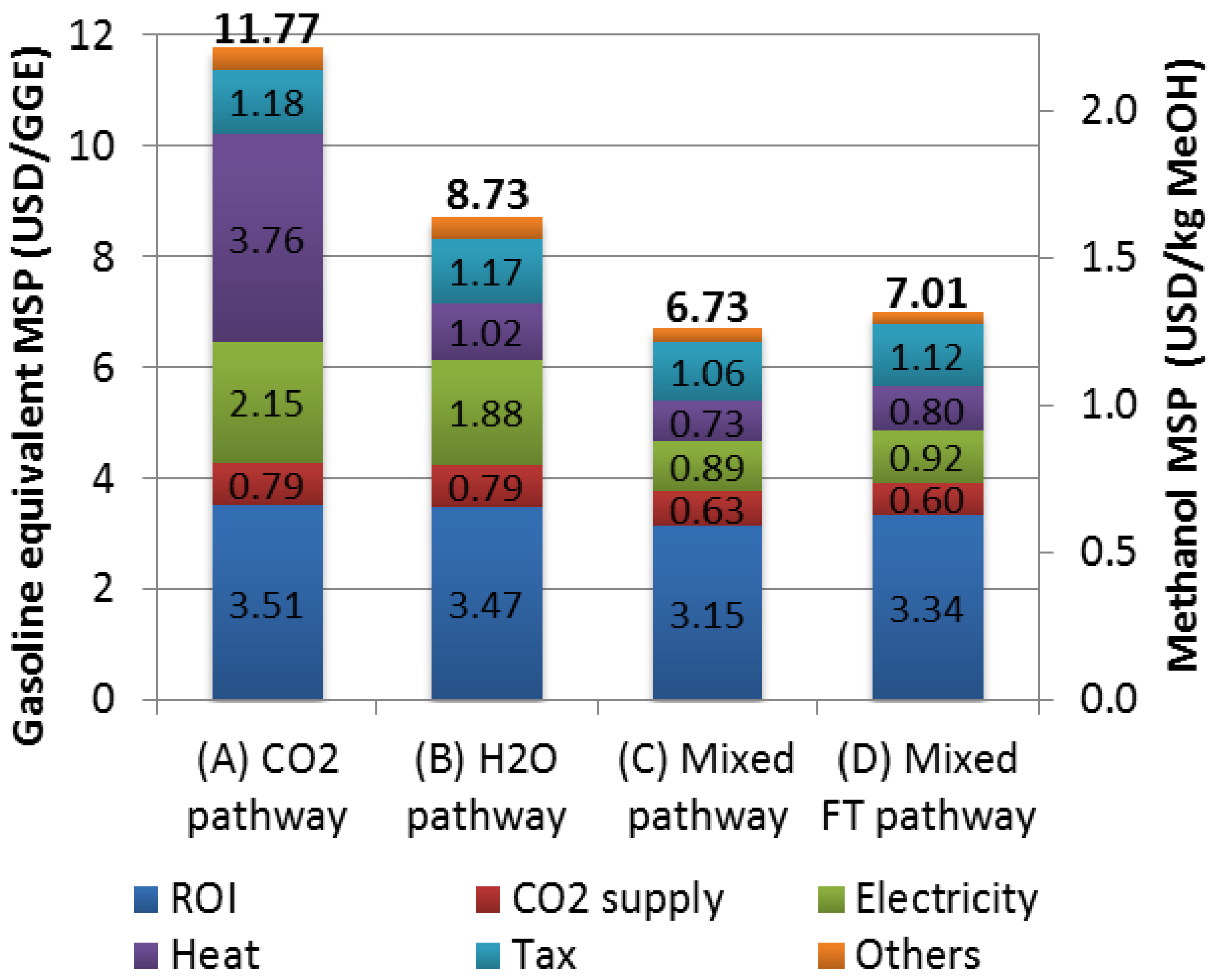
Profit =Earnings after tax - ROI (Return On Investment)

← Economic assumptions

Minimum selling price (MSP) estimation

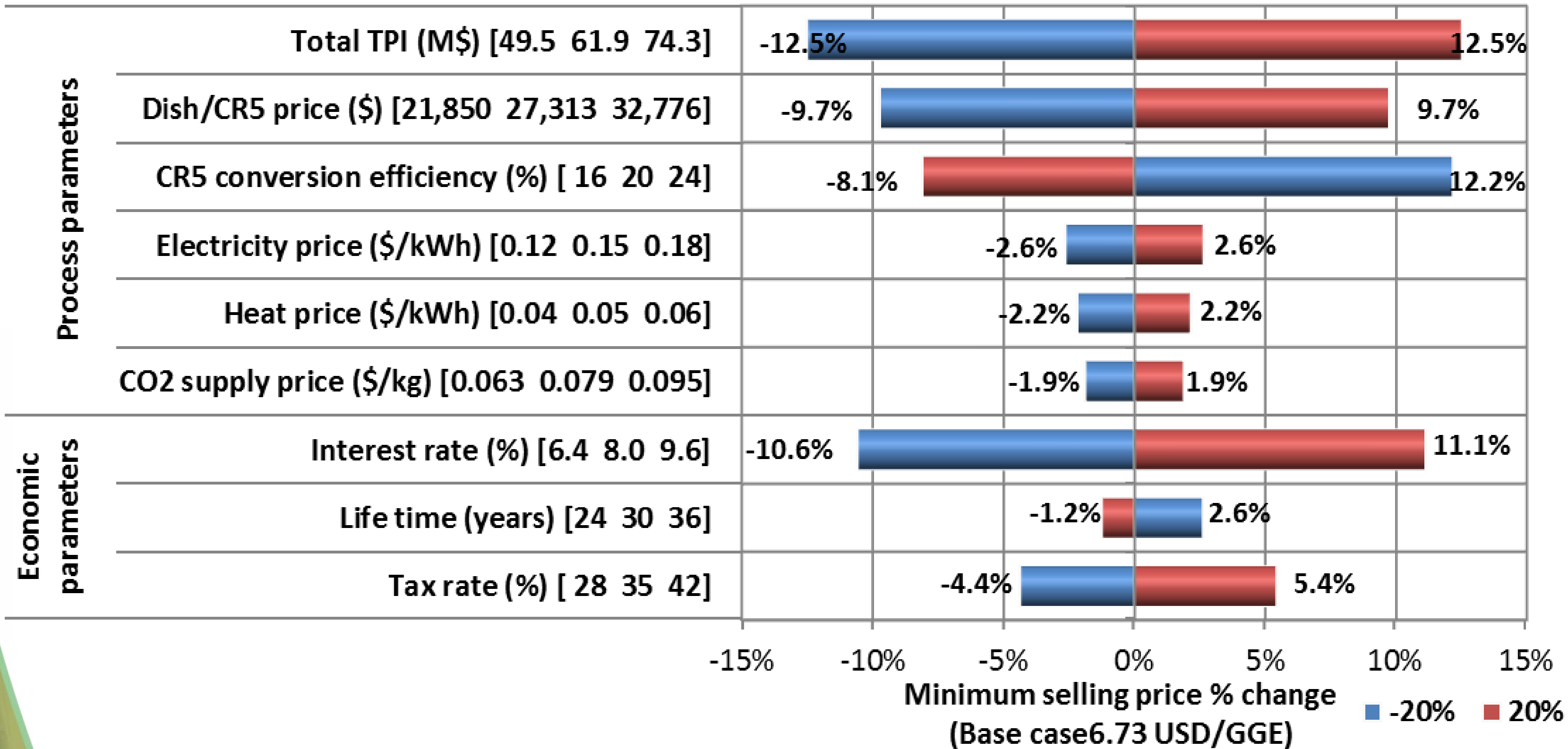
MSP is the price which makes profit equal to zero.

Economic Evaluation: Minimum Selling Price



Economic Evaluation: Sensitivity Analysis

Mixed pathway to MeOH



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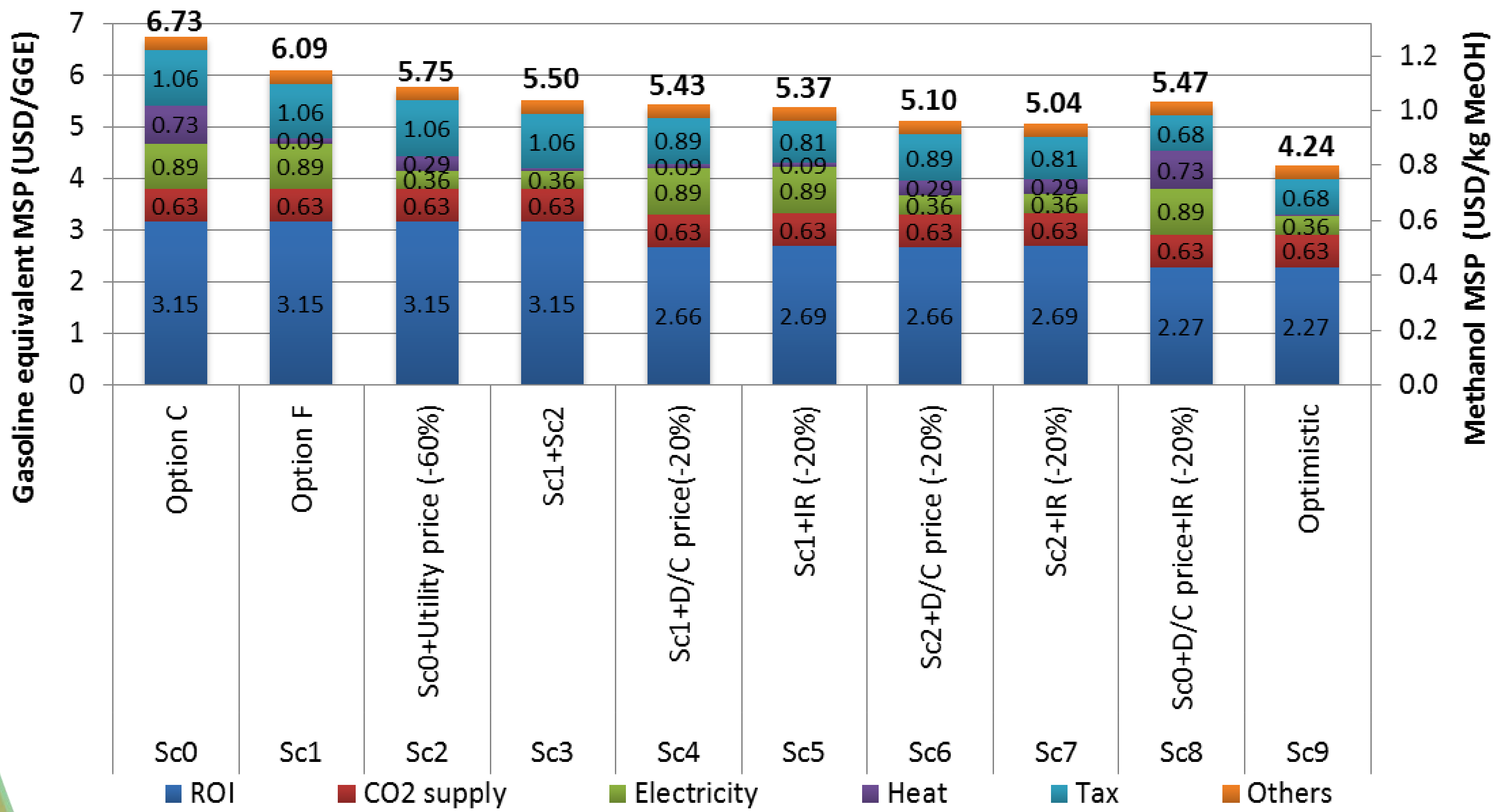


Can 20% or better be achieved?
Efficiency: Solar to Thermal

Resource efficiency = 95% for Daggett, CA (DNI > 300W/m^2)

Operational ~ 94%
Equip. Availability = 97%, Blocking&Shading = 98%, Wind Outage = 99%

Optical ~ 79%
Reflectivity = 93% (two reflections)
Dirt = 95%
Window = 95%
Tracking = 99%
Intercept = 95%

Receiver ~ 82%
Radiation = 82%
Conduction/Convection = 0 %

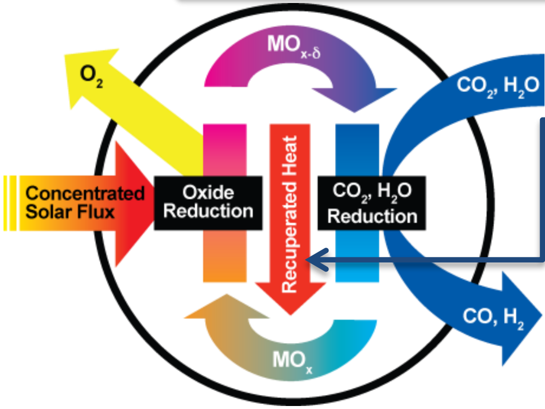
Solar-to heat: ~58%

Solar to Fuel = 10%
If Heat to Fuel = 17%

Nathan P. Siegel, James E. Miller, Ivan Ermanoski, Richard B. Diver, and Ellen B. Stechel “Factors Affecting the Efficiency of Solar Driven Metal Oxide Thermochemical Cycles” Industrial and Engineering Chemistry Research dx.doi.org/10.1021/ie400193q

20%? Thermal to Chemical Efficiency

$MO_x \rightarrow MO_{x-\delta} + \delta/2\ O_2$ (ΔH_1, T_{high}, e.g. 1500 °C)



$MO_{x-\delta} + \delta\ CO_2 \rightarrow MO_x + \delta\ CO_2$
T_{low}, e.g. 800 °C

<u>Efficiency is a function of:</u>

Thermodynamics: ΔH_1 (T_{high} & T_{low}), δ

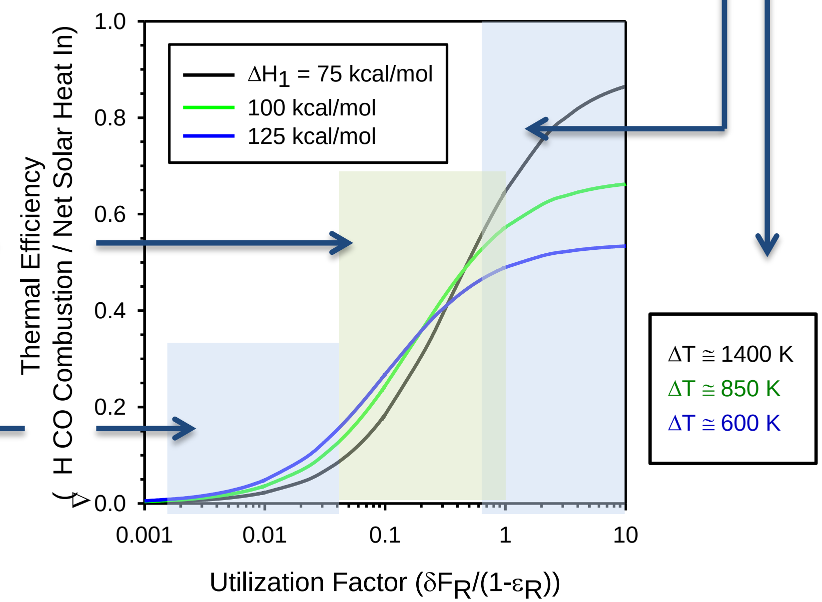
Kinetics: δ

The reactor: recuperation effectiveness & pressures

The maximum possible efficiency is limited by ΔH_1.
High efficiency (small ΔH_1) corresponds to a large T_{high}-T_{low}.

The possible efficiency increases with degree of reaction (δ) and/or effectiveness of recuperation.

When utilization is low, sensible heat demand becomes a more dominant factor than ΔH_1.



Technical Summary

- Plausible route to Solar Fuels – if efficiency is high enough – 10% solar to hydrocarbon minimum.
- Within the scale of other human endeavors
- Costs are “in the ballpark” of competitiveness.
- Capital cost is a primary driver
- Improvements are needed in separations
- Advances in thermochemistry required but plausible – focus on utilization (recuperation and reaction extent).
- LCA work to be published soon.

Lessons Learned

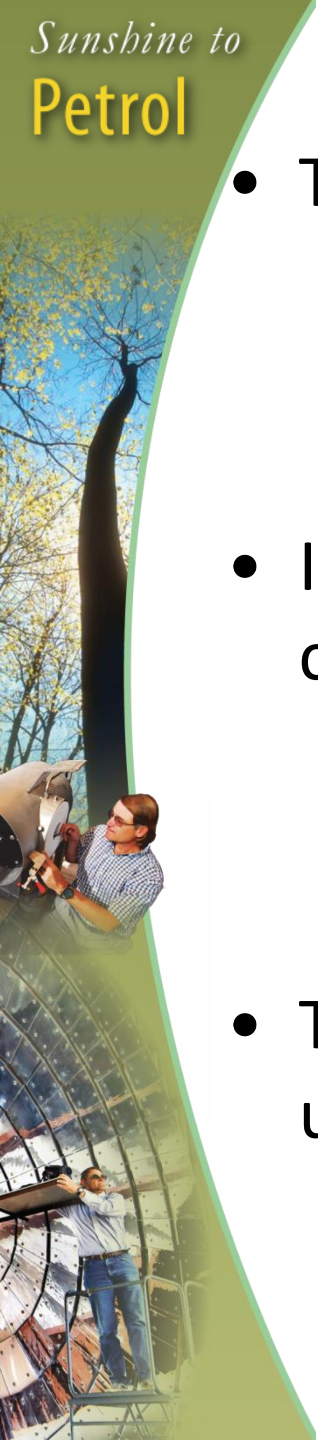
In an Ideal World

- The Vision
- The Big Picture
  - If we succeed, does it matter?
  - If so, under what circumstances
- The Technology
  - Syngas
  - Full system context
  - Thermochemistry

Concurrent efforts are not uncommon

Reality is less linear

- The Vision
- The Big Picture
  - If we succeed, does it matter?
  - If so, under what circumstances →
- The Technology
  - Syngas
  - Full system context
  - Thermochemistry



Underappreciated

- The big picture matters:
  - End to End is critical – BOP matters
  - “efficiency can be low if cost is low” breaks down
  - Efficiency needs to be defined back to the source
- Important to state assumptions, work from a common basis
  - Necessary for good decision making
  - Avoid creating false expectations that undermine the enterprise in general
- There are disincentives for a research effort to undertake this type of work
  - more difficult as work becomes more collaborative, cross discipline, blurs the lines of basic and applied…

Challenges

- What do we assume about the future?
  - "When will this be competitive" is a loaded question assuming no changes in the status quo.
  - Externalities, regulations …
  - What do we assume about other technologies? - In our case "where does the CO_2 come from?"
- How do we compare across technologies
  - Energy is not energy is not energy …
  - Biomass looks to capital investment per unit capacity – the feedstock solar fuels largely appear as capital
  - What metrics are important and how are they valued? water, land, security, CO_2 … ($, social costs, etc?)
- How do we use this tool to set targets, goals, and expectations without discouraging innovation?