The Dual-Fuel Strategy
An Energy Transition Plan

William Ahlgren
Electrical Engineering Department
California Polytechnic State University
San Luis Obispo, CA 93407-0355
wahlgren@calpoly.edu

Perspective on global warming

- Compelling evidence
- Consensus of expert opinion
- Downside risk is overwhelming
- Risk mitigation is prudent

We need a plan to phase out fossil energy

Energy sources

- Fossil
- Renewable
- Nuclear

Energy sources are converted to energy vectors to enable trade

Energy vectors

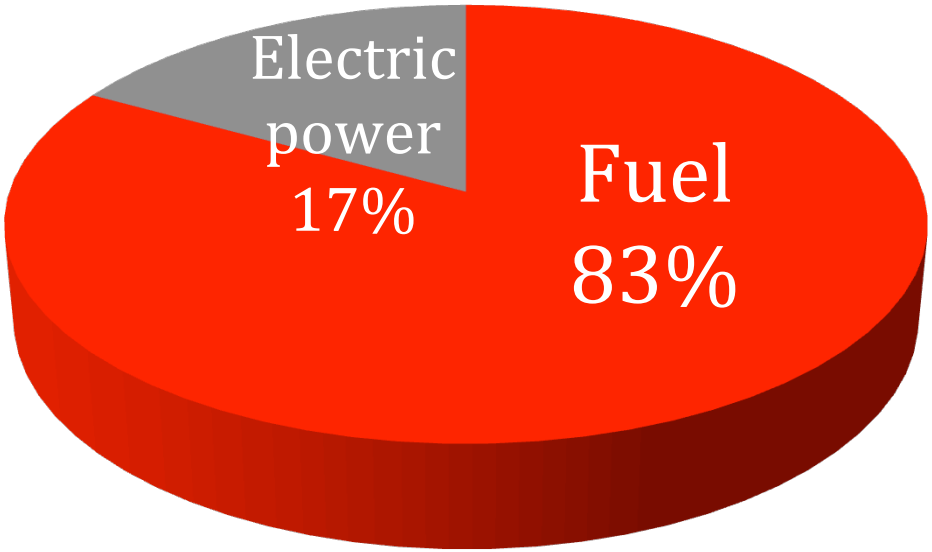
- Fuel
- Electric power

A vector is an energy carrier that can be bought and sold

Source and vector are distinct!

- Oil and natural gas are fossil *sources* that are often used to make fossil *fuels*
- But they can also be used to make *renewable* fuels
- Natural gas is used to make hydrogen, ammonia, and methanol

Fuel dominates energy trade



Fuel is crucial in the global energy system. Replacement by electric power with non-fuel storage is unlikely.

Renewable fuel is key

- Fossil → Fuel + Electricity
- Renewable
- Nuclear

} → Electricity

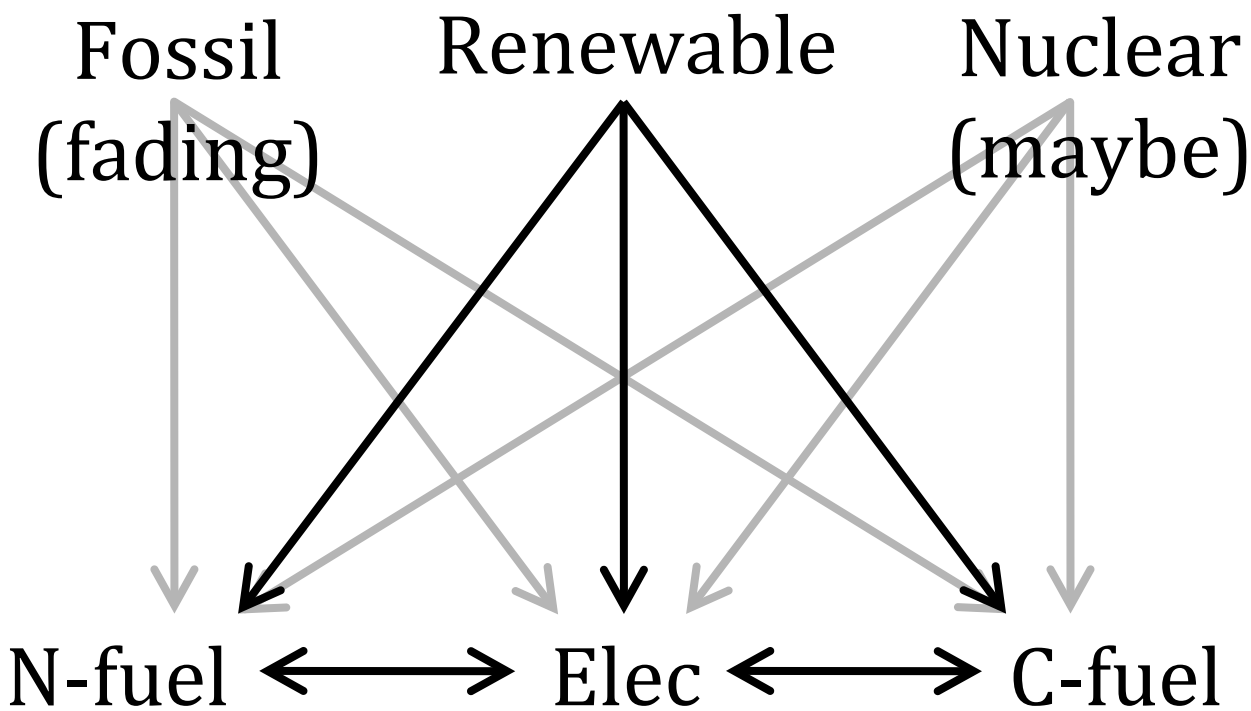
Fossil fuels come only from fossil sources.

Transition to renewable sources requires renewable fuels.

Source-neutral vectors

- Electric power can be produced using any energy source
- Renewable fuels must also be source-neutral
- E.g. three vectors:
  - Electric power
  - Nitrogen-based fuel: N-fuel
  - Carbon-based fuel: C-fuel

Sustainable global energy system



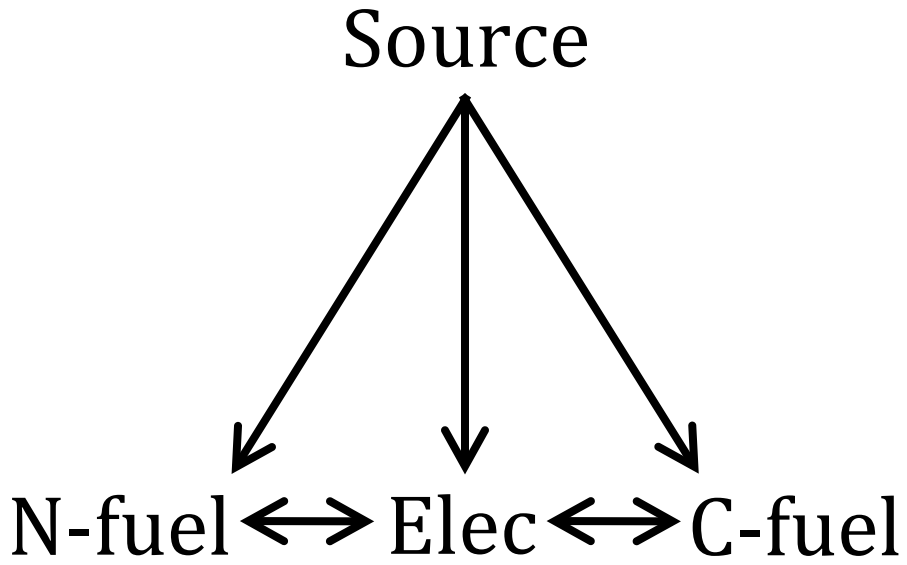
Highly inter-connected source-vector network makes for stable supply at low cost

Nuclear, maybe

- Subsequently I use “Renewable” as short-hand for “Renewable and maybe nuclear.”
- Nuclear energy might play a role.
  - Fusion
  - Safe and sustainable fission, e.g. Liquid Fluoride Thorium Reactor (LFTR)*
- If so, plants will be sited remotely from population centers.
- Energy must be stored and transported as fuel.

* Web site: Energyfromthorium

Dual-fuel energy triangle



All energy trade is carried by two (or few) renewable fuels plus electric power, inter-convertible with each other.

Fossil-free energy

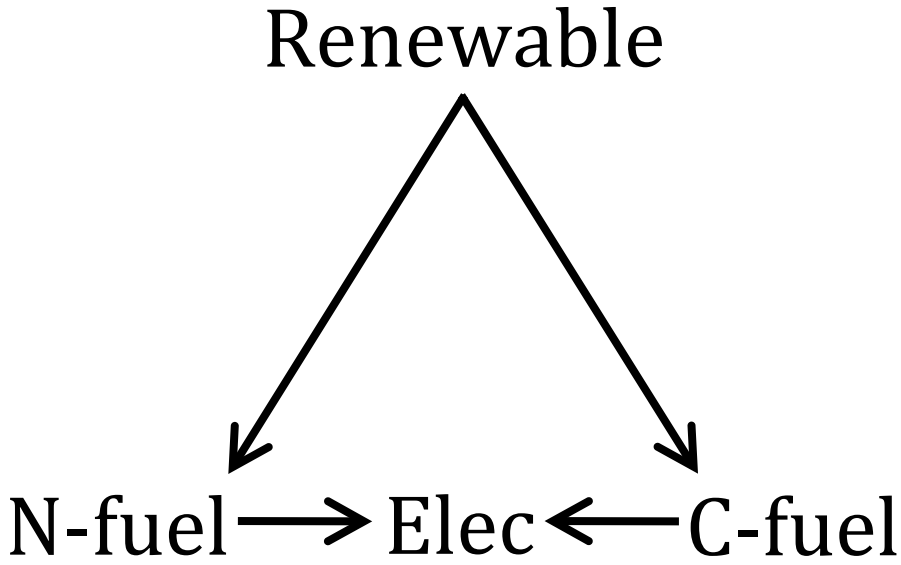
Renewable

↓

N-fuel ↔ Elec ↔ C-fuel

Renewable (and maybe nuclear) sources generate electric power used to produce renewable fuels

And/or…



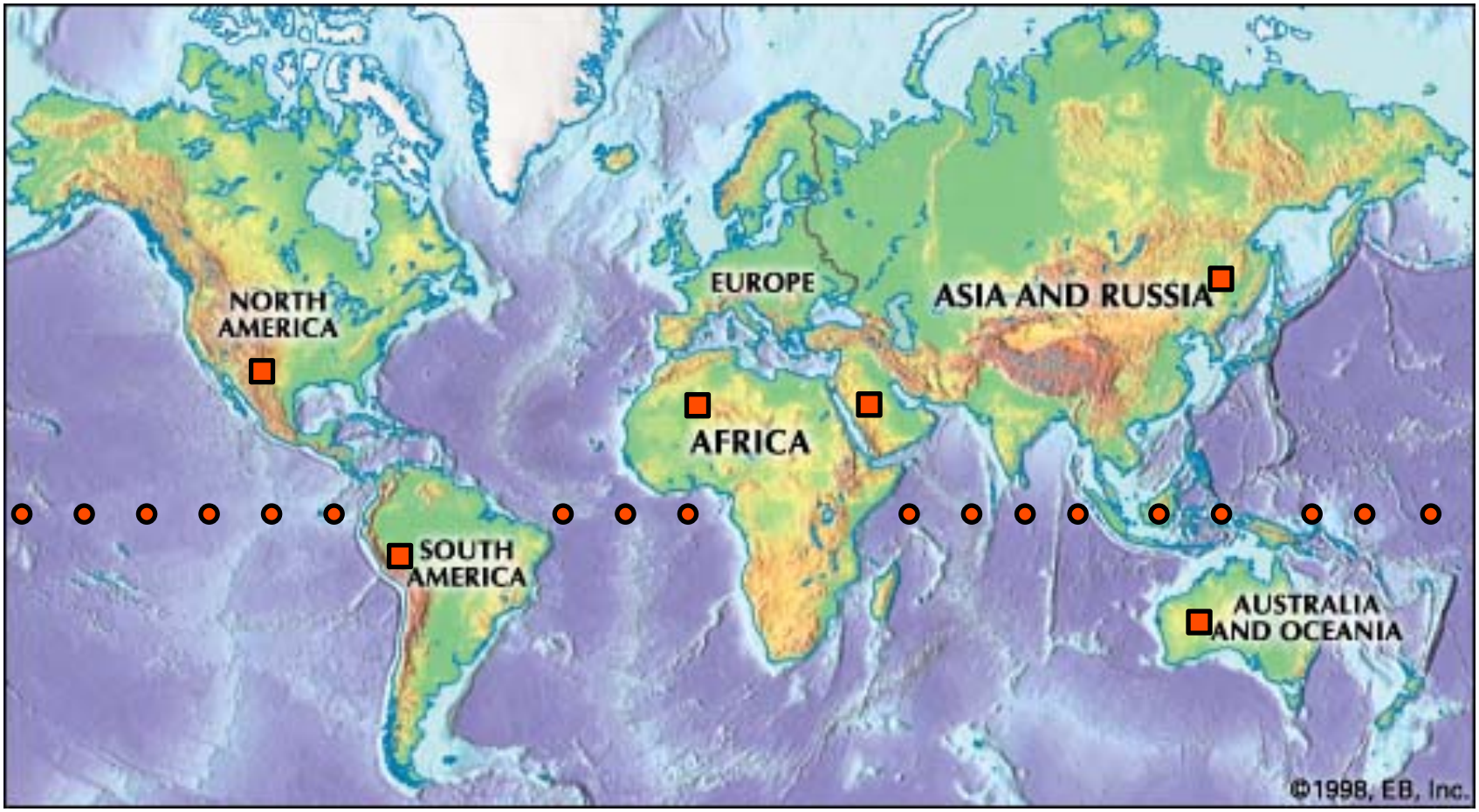
Direct conversion to fuels; subsequent conversion to electric power for use.

Solar is the big energy resource

- Rooftops might supply 10% of global energy
- The rest must come from energy farms
- All sizes, located everywhere
- Very large energy farms will be built in remote deserts and oceans

Transport and storage of renewable or nuclear energy captured in remote energy farms will be accomplished using liquid renewable fuels

All we need is 2% of Earth surface



Adapted from Nate Lewis, *Powering the Planet*.

Fossil fuels are hard to displace

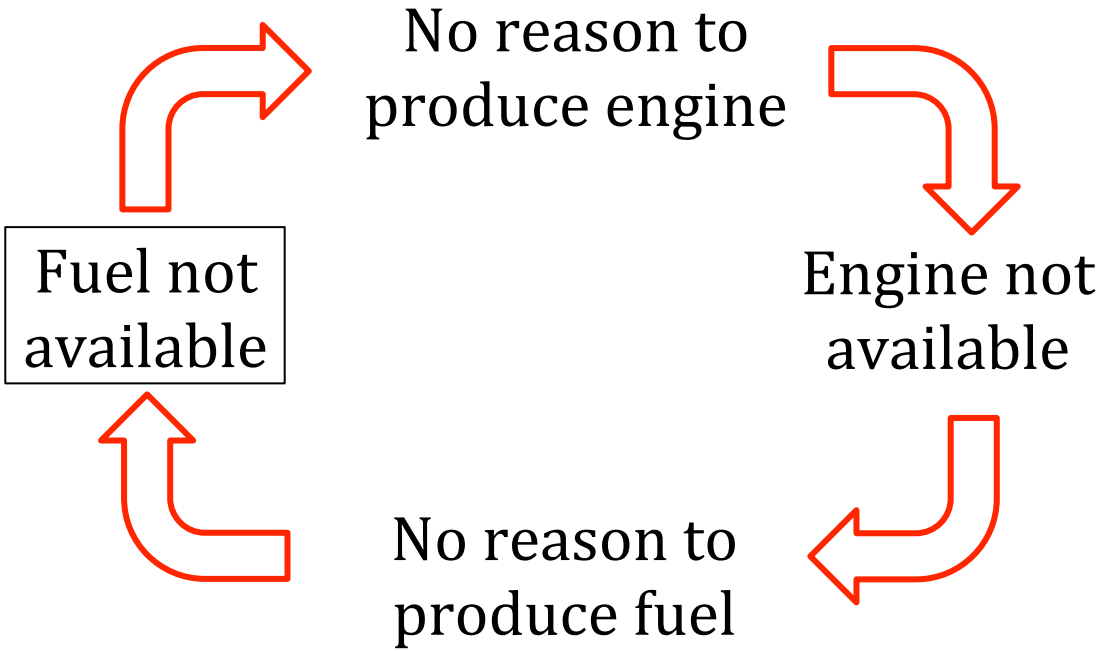
1. EROI –falling
2. Economic inertia

Economic inertia created by legacy infrastructure. To compete, renewable fuels must be compatible —liquids!

Legacy infrastructure

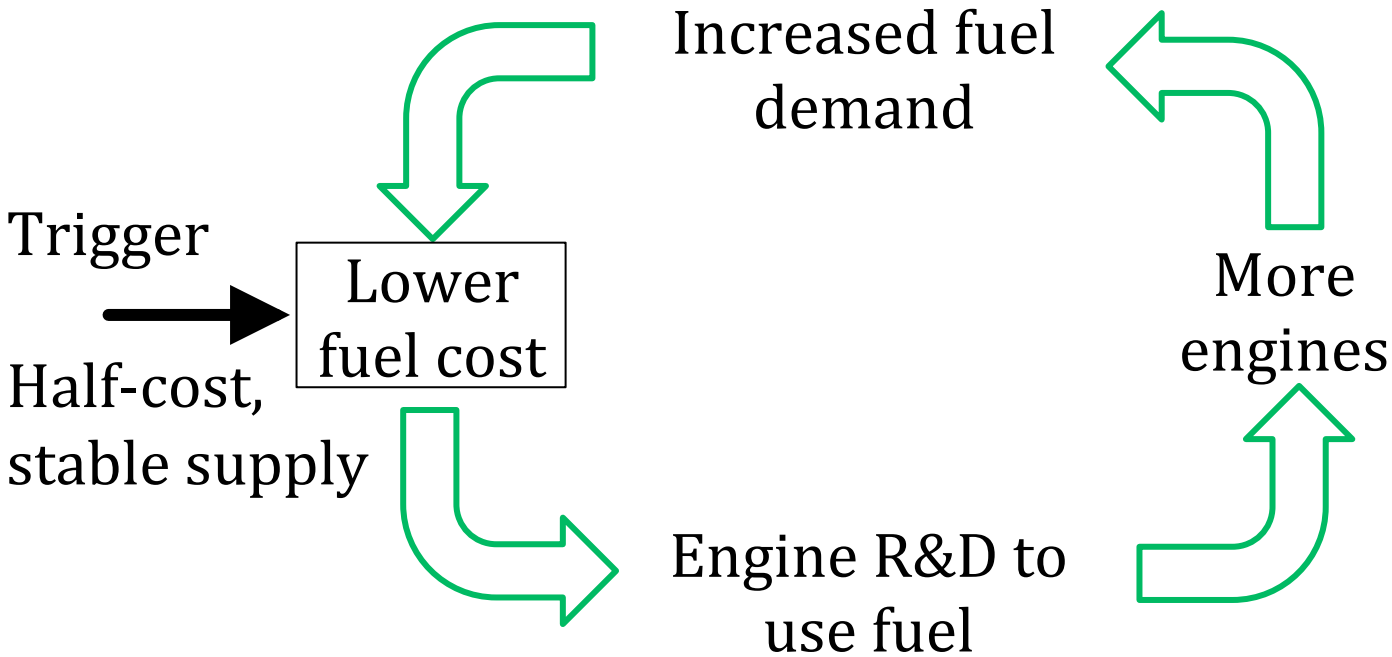
- Pipelines
- Tankers—sea, river, rail, road
- Storage—tanks
- Combustors—furnaces and boilers
- Engines—GTs and ICEs

Feedback prevents change



Status quo is stabilized in a <u>vicious</u> cycle: economic inertia.

Feedback will enable change



Change is driven by a virtuous cycle after a threshold stimulus is applied

Trigger

Liquid renewable fuels with

- stable supply
- *one-half* cost per energy unit

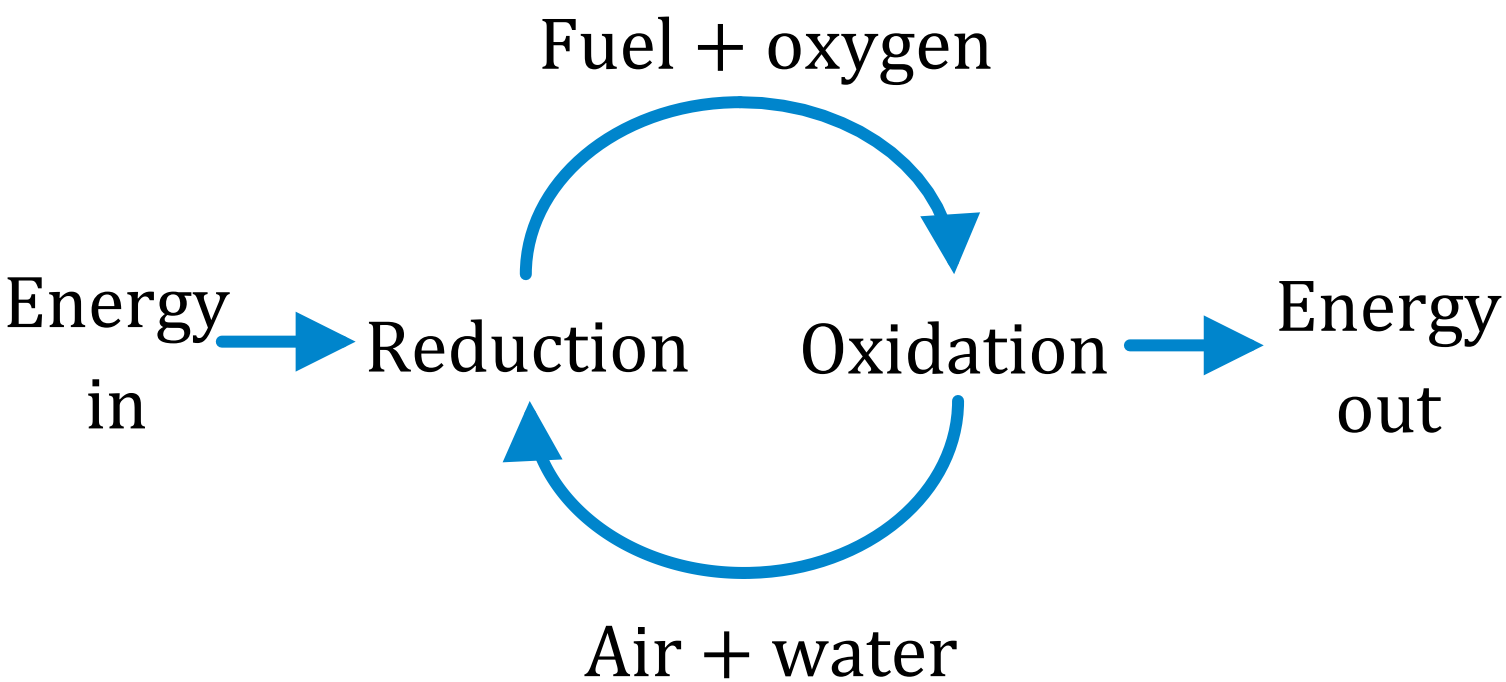
…compared to competing fuels

Strategy

- First produce renewable fuels from natural gas and perhaps coal. Compared to oil:
  - Stable supply
  - Half-price per energy unit
- Create market demand for renewable *fuels*
- Demand stimulates innovation and investment in production from renewable *sources*
- Cost of production from renewable sources goes down
- Renewable sources then displace fossil sources

We need liquid renewable fuels. What are they?

Renewable fuel cycle



Air and water

N_2

O_2

CO_2

H_2O

Renewable fuel options

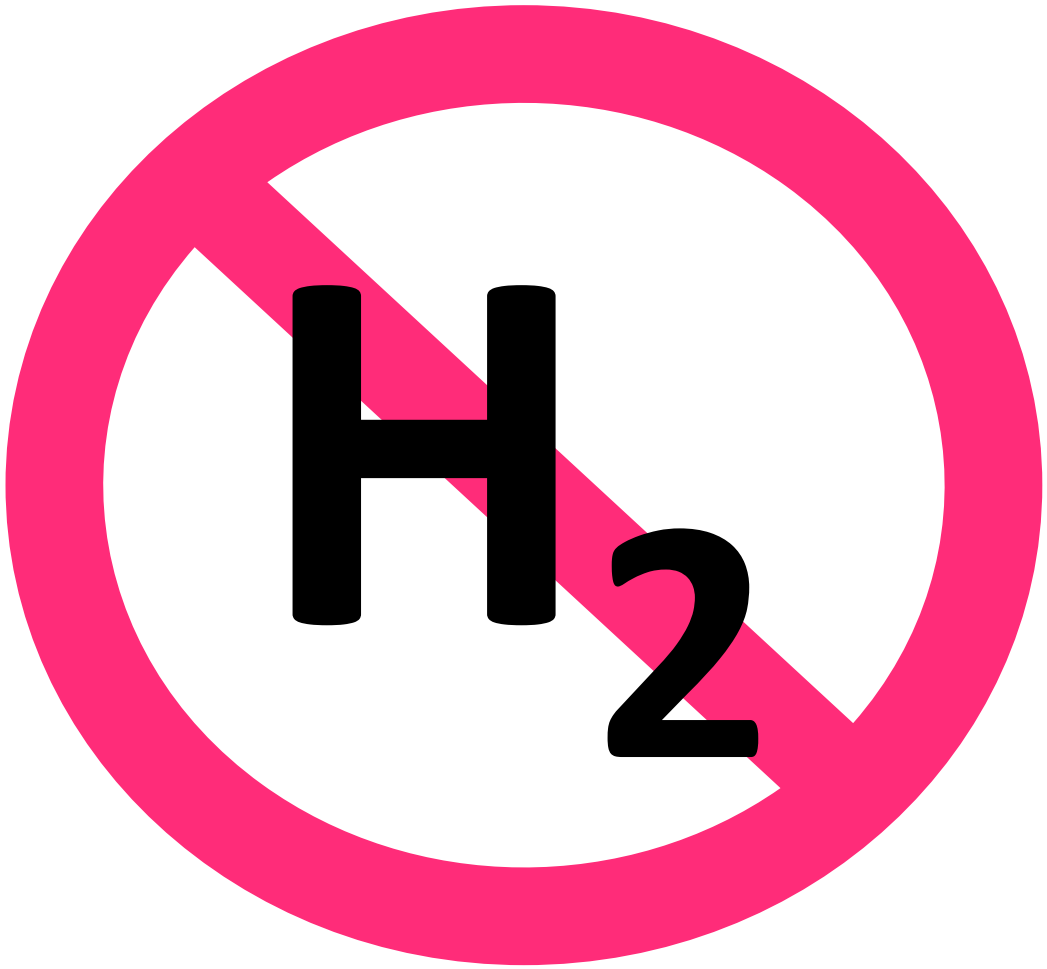
Reduction
$\rightleftarrows$
Oxidation

- Hydrogen $H_2O \rightleftarrows H_2 + \frac{1}{2}O_2$
- Ammonia $\frac{1}{2}N_2 + \frac{3}{2}H_2O \rightleftarrows NH_3 + \frac{3}{4}O_2$
- Methanol $CO_2 + 2H_2O \rightleftarrows CH_3OH + \frac{3}{2}O_2$

State of the Hydrogen Economy

- 40+ years intense effort
- Still no Hydrogen Economy
- Why? Perhaps:

Hydrogen is incompatible with existing infrastructure because it is a high vapor-pressure gas.


H_2

Ammonia-methanol dual-fuel pair

- Ammonia is **carbon-free**…

  …but high relative toxicity

- Methanol is **low relative toxicity**…

  …but contains carbon

- They are complementary:

  Each has strength to compensate the other's weakness

Better alternatives?

- *Nitrofuel* is nitrogen-based renewable fuel
  - NH_3 is the simplest example
  - Liquid ammoniates (e.g. Divers' solution) may be better
  - Key feature: *zero (or low) carbon*
- *Carbofuel* is carbon-based renewable fuel
  - CH_3OH is the simplest example
  - Others (e.g. EtOH, DME, CNHCs) may be better
  - Key feature: *low relative toxicity*
  - CNHCs offer *high energy density*

N-fuels cost less than C-fuels

Air 78% N_2 ⇒ N-fuels are low cost
Air 0.04% CO_2 ⇒ C-fuels are high cost

$ NH_3 – low energy density/professional handlers
$$ CH_3OH – low energy density/nonprofessional
$$$ CNHCs – when high energy density is mandatory

Use NH_3 when possible; CH_3OH when necessary; CNHCs when essential.

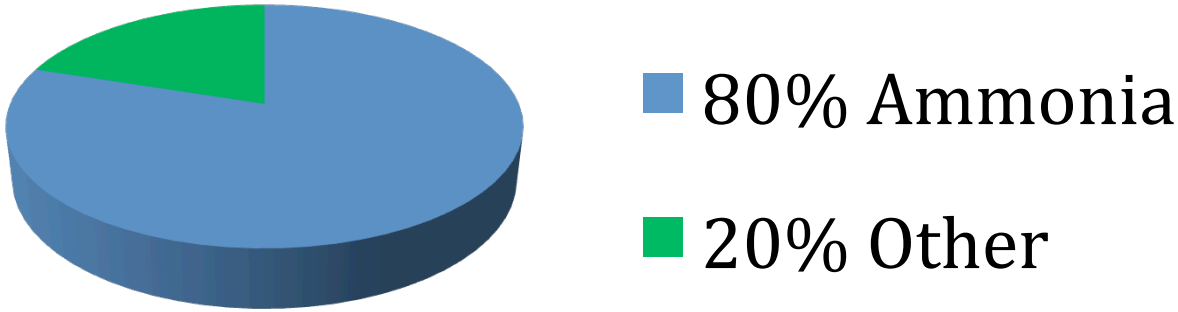
Highest cost: CNHCs

Carbon-Neutral Hydrocarbons

- Examples:
  - higher alcohols (e.g. butanol)
  - higher alkanes (e.g. octane, dodecane, hexadecane)
- Produce from air-derived synthesis gas or methanol
  - E.g. Fisher-Tropsch or Mobil MTG processes
- Direct replacement for fossil fuels
- High energy density and also high cost

Use when energy density justifies cost
–e.g. aviation (perhaps)

Nitrogen-based fuel meets most needs



"20% other" includes:

- Methanol for non-professional highway transport
- CNHCs for high-energy density (e.g. aviation)

Ammonia issues

- Inhalation hazard
- Fire/explosion advantage
- Environmental risks
- NOx

Personal Protective Equipment (PPE) Requirements For Ammonia

REQUIRED

RUBBER GLOVES

RECOMMENDED

FACE SHIELD
(not a substitute for goggles)

REQUIRED

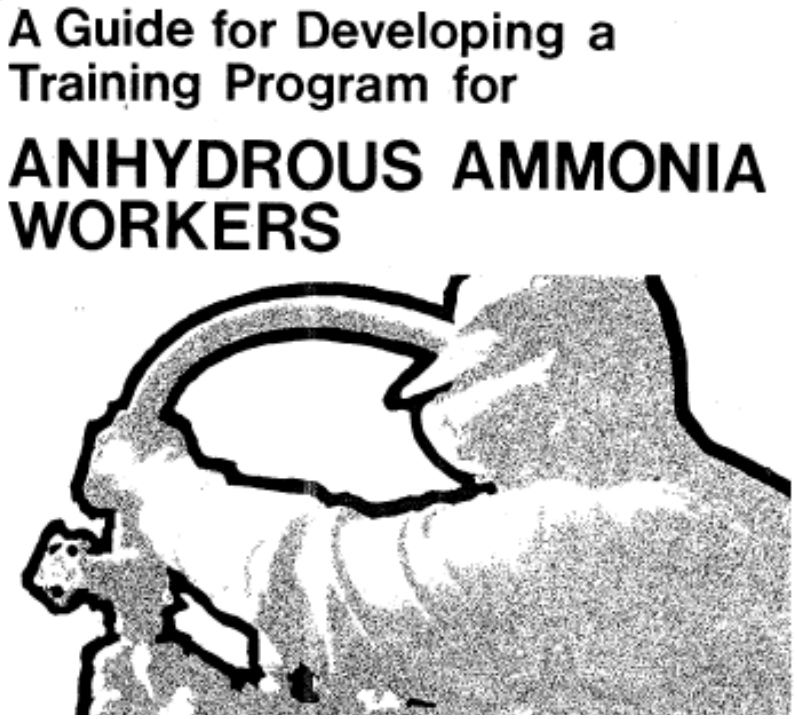
EYE PROTECTION

RECOMMENDED

LONG SLEEVE SHIRT

SAFE Safe Ammonia Facilities Education

Mandatory training every two years



Safety advantage of NH_3

Low fire/explosion hazard

- NFPA/DOT class "non-flammable"
- Anomalously high minimum ignition energy (MIE) in air
- Ideal fuel for fire/explosion safety:
  - Can be ignited in a combustor
  - Very difficult to ignite accidentally
  - Lighter than air—rises and disperses
  - Flame extinguished by water

Environmental risks

NH_3 spill effects are intense but short-lived

- Ammonia in high concentration is toxic
- In low concentration, it's fertilizer
- Spills disperse and self-remediate relatively quickly compared to oil
- Nitrification is a risk—mitigation is required
- NH_3 is inferior to H_2 in this category, but H_2 has other issues ...

There is no perfect fuel; all have pros and cons – assess choices relative to each other

NOx

- Thermal NOx comes from heating air; forms no matter what fuel—even hydrogen

$$N_2 + O_2 + \text{heat} \rightarrow 2NO$$

- Fuel-bound nitrogen can form NOx more easily; single vs. triple bond to break
- Both controlled by kinetics not thermodynamics
- Both suppressed by combustion engineering
- True for *any* fuel, including ammonia

Thermal de-NOx

$$NH_2 + NO \rightarrow N_2 + H_2O$$

- NH_3 injected after burner to suppress NOx
- NH_2 radicals act as scavenger
- Invented mid-seventies—Exxon patent
- Now used in most fossil-fueled electric power plants, which have ammonia on-site

Low-NOx ammonia combustion is possible but requires careful engineering

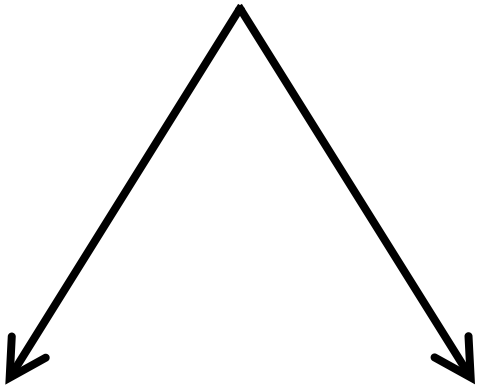
Fuel production

- Petrochemical (chemical-to-chemical)
- Thermochemical (heat-to-chemical)
- Photochemical (light-to-chemical)
- Electrochemical (electric-to-chemical)

Petrochemical

Current low-cost standard for production of ammonia and methanol

Natural gas
(or coal or oil)



Ammonia

Methanol

Thermochemical

Direct path from solar thermal and nuclear to renewable fuels

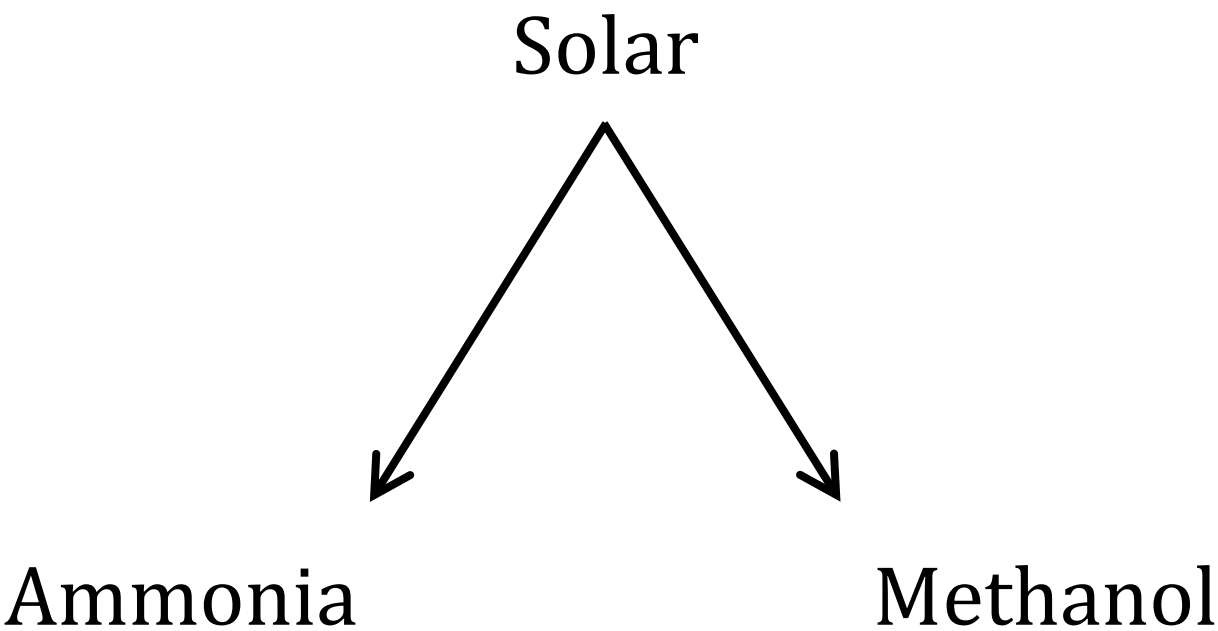
Solar thermal
(and maybe nuclear)

Ammonia

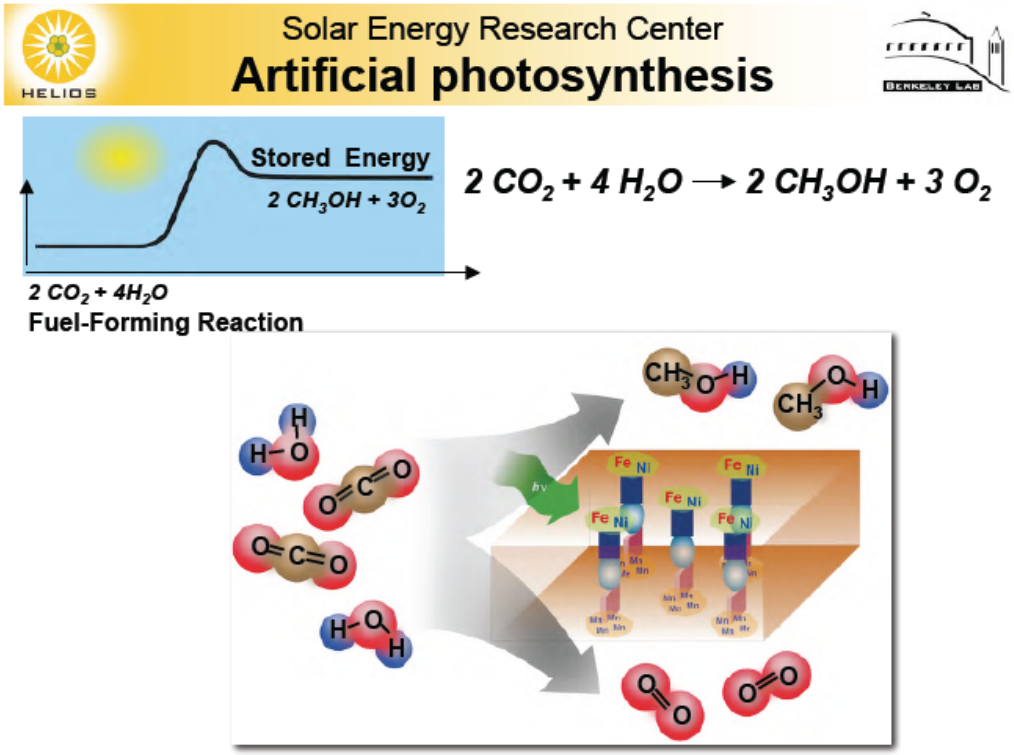
Methanol

Photochemical

Direct path from solar to renewable fuels



Example from LBNL



Applause!

Electrochemical

An indirect path through electric power

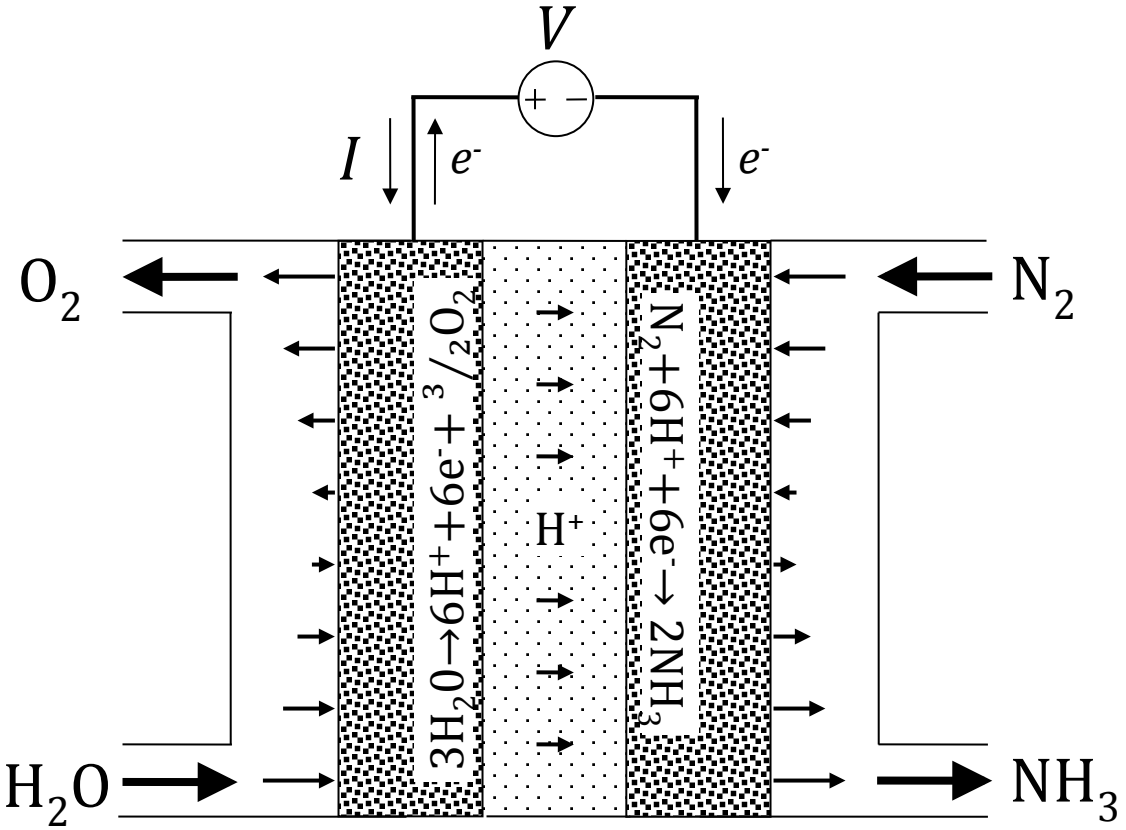
Wind, Solar PV

↓

Ammonia ⟷ Electric power ⟷ Methanol

Example: HTEC

High-temperature electrochemical conversion using proton-conducting solid electrolytes

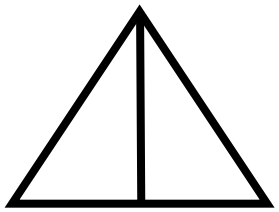


Efficiency target: 80%

- 80% efficiency each-way conversion of electric power to and from chemical energy (fuel)
- Theoretically possible
- Challenging!
- But imagine: what will happen if this is achieved?

High-efficiency two-way electrochemical energy conversion based on liquid renewable fuels is
DISRUPTIVE TECHNOLOGY.

Dual Fuel Exchange: DFX



A sustainable energy-trade system:

- Two (or few) renewable fuels plus electric power
- Dual use of legacy infrastructure
- Source-neutral fuel production

DFX enables renewable energy sources

Competitive advantage

Liquid renewable fuels vs. oil-derived fuels

- Agile production
  - Source-neutral
  - Low-cost, stable supply
- Legacy compatibility
  - Renewable fuels, like current fossil fuels, are *liquids*
  - Low investment barrier to adoption
- Risk mitigation
  - Global warming
  - Regulatory actions

Strategy

- To begin, market renewable fuels produced at low-cost from fossil sources
- Identify trigger markets in which renewable fuels can best compete
  - Maximum benefit from stable supply at low cost with low carbon footprint
  - Minimum infrastructure investment barrier
- Grow market for renewable *fuels*
- Transition to renewable *sources* as technology develops enabling low cost

Renewable fuels from fossil sources

- Standard practice today
- GTL/CTL gives competitive advantage
- Trigger transition to DFX

It costs energy to convert NG to ammonia/methanol. Why do it?

- Liquids are easy to transport and store
- Stranded NG can be monetized
- Safety advantage—low explosion hazard
- Carbon advantage—no CO_2 emissions from ammonia at the point-of-use

⇒ *Lower cost delivered to consumer*

Half-price threshold is within reach

2009 cost estimates

Fuel	P (bar)	Density ($kg \cdot L^{-1}$)	HHV ($MJ \cdot kg^{-1}$)	Energy density ($MJ \cdot L^{-1}$)	Cost per volume ($CN\$ \cdot L^{-1}$)	Cost per energy ($CN\$ \cdot GJ^{-1}$)
Ammonia	10	0.603	22.5	13.6	0.18	**13.3**
CNG	250	0.188	42.5	10.4	0.23	28.2
LPG	14	0.388	48.9	19.0	0.55	28.5
Methanol	1	0.786	22.7	17.8	0.42	**23.5**
Gasoline	1	0.736	46.7	34.4	1.00	29.1
Hydrogen	14	0.025	142	3.6	0.10	28.2

1 gal
= 3.8 L

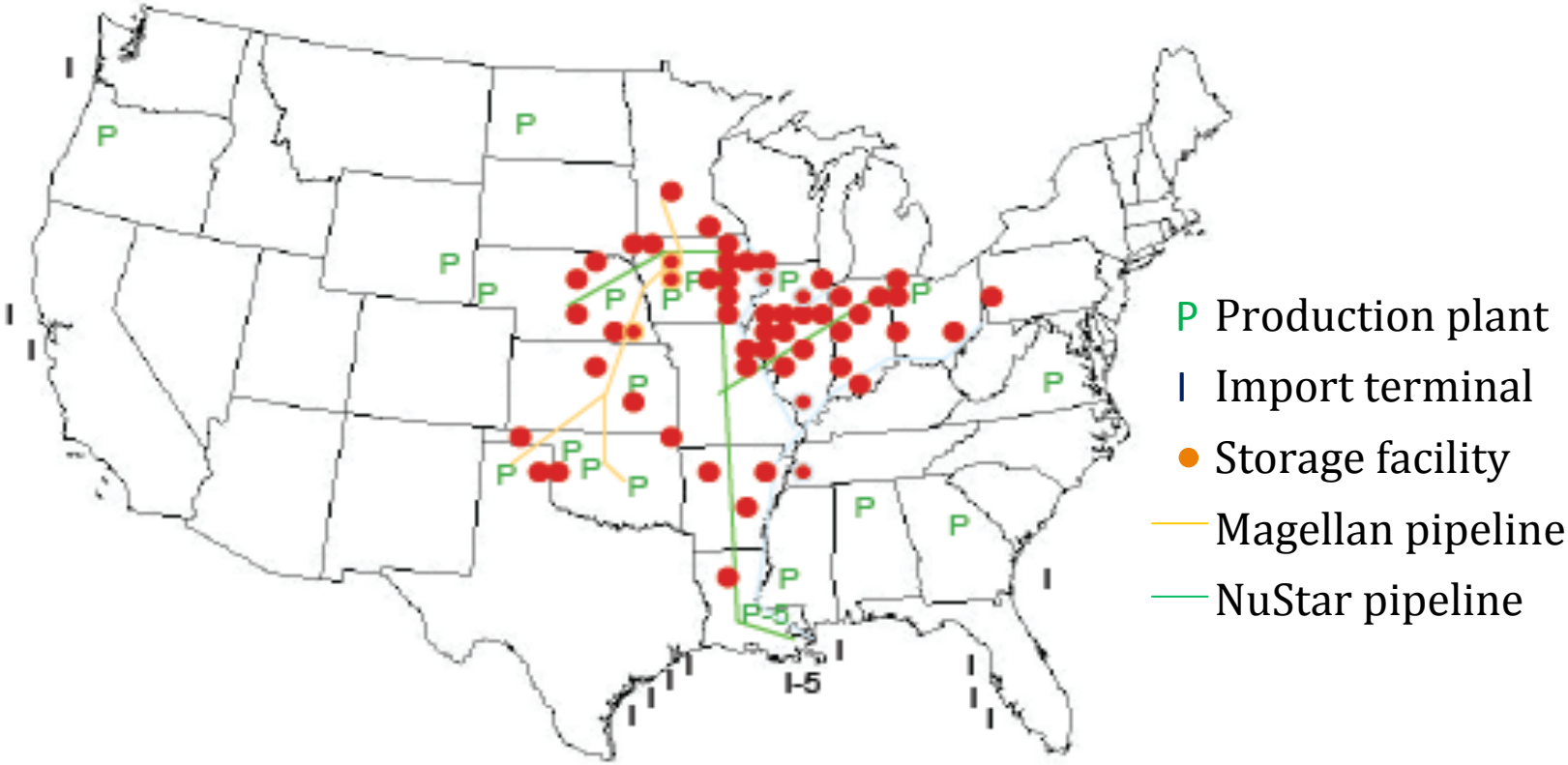
C. Zamfirescu and I. Dincer, "Ammonia as a green fuel and hydrogen source for vehicular applications." *Fuel Processing Technology* 90: 729–737 (2009). Hydrogen storage as metal hydride is assumed. Methanol specific energy restored from reformer-adjusted to true value.

Trigger markets for ammonia

- Base load electric power; especially near existing ammonia pipelines
- Energy hubs; CCHP (trigeneration)
- Rail and marine propulsion; trains and ships can carry enough fuel for long trips with them

These applications employ professional fuel handlers

U.S. ammonia infrastructure



Ray Hattenbach, Chemical Marketing Services Inc., 2006

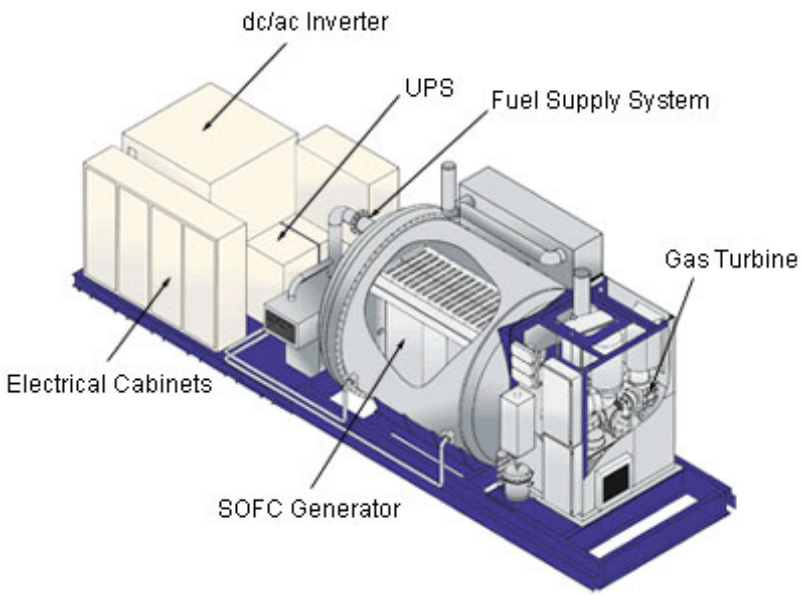
Gigawatt power generation

Replace natural gas with ammonia

- Only the boiler needs modification
- Ammonia is already familiar to power plant operators (thermal denox)

DG–CCHP

Distributed Generation with Combined Cooling Heat and Power



High efficiency electric power generation by utilizing otherwise wasted heat.

Energy hubs

Power and energy paradigm for the 21st century

- Energy hubs both *produce* and *consume* energy; trade between hubs to balances production/consumption
- Very high efficiency is achieved by DG-CCHP (DTG: Distributed Tri-Generation)
- Trade between hubs is carried by *both* electric power and renewable fuels; new "Grid" is a network for both
- Some hubs *produce* fuels, others only consume
- Energy moves by land in wires and pipes (or river, rail and road tankers) and by sea in tanker ships
- Energy is stored as liquid renewable fuels in low-cost tanks, *definitively solving the storage problem for renewable sources*

Fuel power density

Figure of merit for pipeline transport of fuels

$$F = \rho h \sqrt{h}$$

Name	Formula	M	p	ρ	h_H	h_L	ρh_L	$\sqrt{h_L}$	F
		g/mol	bar	kg/m^3	MJ/kg	MJ/kg	GJ/m^3	km/s	TW/m^2
Hydrogen	$H_2(g)$	2.02	50	4.06	141.80	120.97	0.49	11.00	5.41
Methane	$CH_4(g)$	16.04	50	35.85	55.50	50.01	1.79	7.07	12.68
Ammonia	$NH_3(l)$	17.03	10	681.90	22.50	18.65	12.71	4.32	54.90

Ammonia is 5× better than natural gas and 10× better than hydrogen

Pipes vs. wires

Low-cost transport by sea

$$$$

$

Monetize stranded natural gas.

West coast port facilities

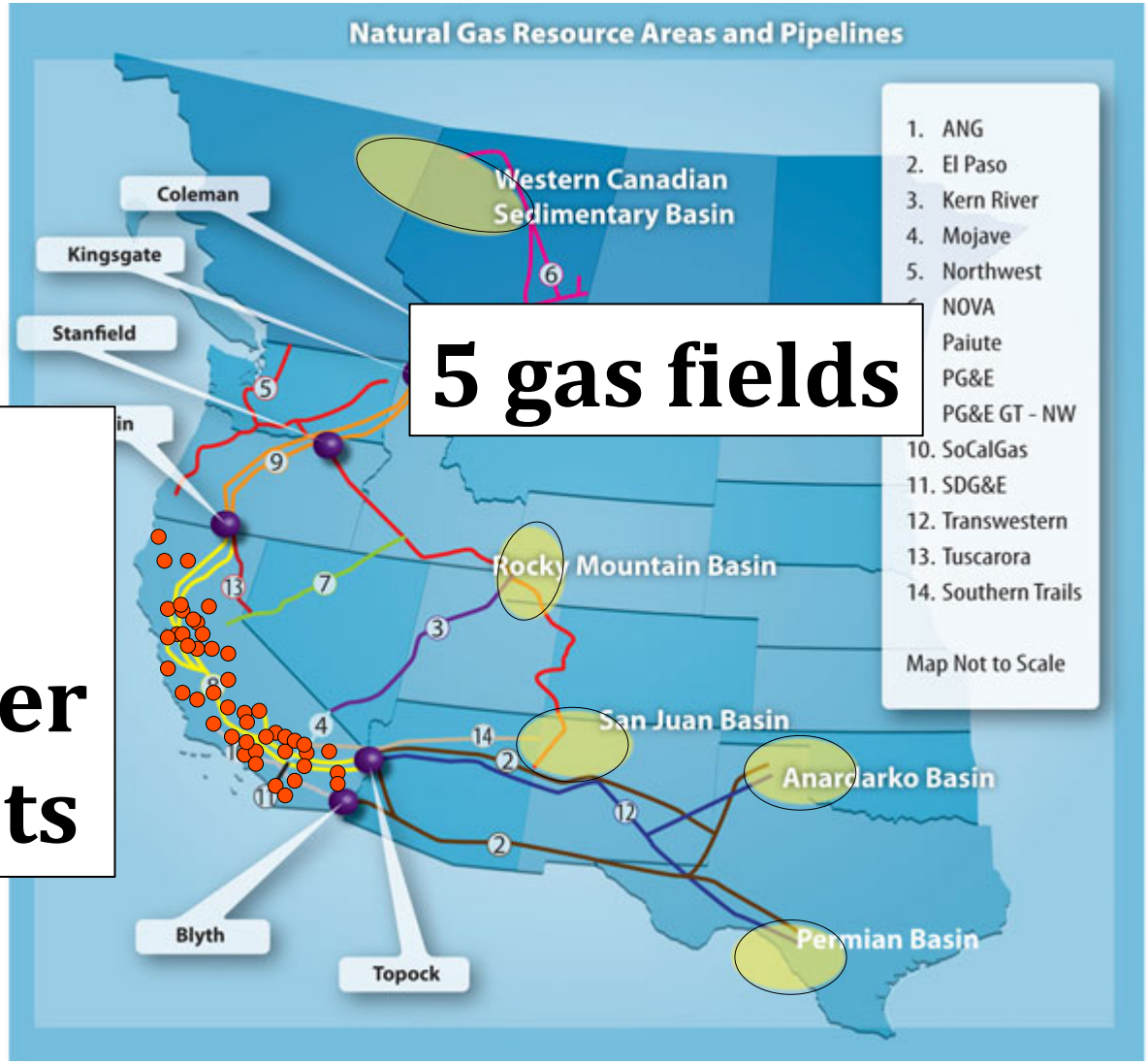
LNG

Ammonia

Near-term CO_2 reduction

Enable CCSS by concentrating CO_2 at a few large sources

California



5 gas fields

390 gas power plants

Marine propulsion

- Ammonia is shipped in tankers
- Why not use it to propel the ship that carries it?
- Why not use it to propel other ships?

Ammonia as fuel for ships

- Distribution relatively easy
  - Ships travel long distances between re-fueling
  - Need only a few marine fuel terminals
  - Low energy density not a major problem—bigger fuel tanks (relatively easy to make bigger ships) or more frequent rendezvous with tenders
- Low pollution
  - NOx can be suppressed (R&D needed)
  - No SOx, CO, CO_2, soot, etc.
  - Small spills rapidly remediated by natural processes—NH_3 is a nutrient in small doses
- Enhanced survivability for warships
  - Fuel supply difficult to ignite
  - If ignited, fire is easily extinguished with water

Conclusion

- Hydrogen as renewable fuel has a fatal flaw: it is a high vapor-pressure *gas*
- Ammonia and methanol have long been known as *liquid* renewable fuels
- Alone, each has it's own flaw that has historically discouraged development
- Together, they are a superior alternative to hydrogen

Thank you for your attention

wahlgren@calpoly.edu

In reply to e-mail I will send a 96-page working paper with 285 references