Overview of the Energy Challenge, and the Science and Engineering of WindFuels/CARMA

Economically Producing Fuels and Chemicals from CO_2, CH_4, and Off-peak Wind

A scalable, competitive energy and climate solution.

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Peak Oil, Peak Coal, Peak Gas, and Peak Uranium are coming.

In June 2008, when petroleum demand briefly came within 1.5% of supply, we had a foretaste of what can be expected after 2014.

Likely Estimates:

Crippling Oil Prices – by 2015

Less recognized:

Peak Coal and Peak Gas - 2030

Biofuels – not scalable

- Their *net* contribution in 2012 – about 0.6% of oil.
- Corn & grain prices increased by 50% in 2012.
- Newly tilled soil creates a "carbon debt" for 30 to 250 years.
- LAND USE – needed for food – for a starving billion.
- Ocean Dead Zones are expanding due to fertilizer run-off.

Under 29% of the carbon in the feedstocks going into cellulosic ethanol refineries ends up in the ethanol. Most of the rest is emitted as CO_2.

Cellulosic ethanol will not compete

- Cellulosic feedstocks (dry, delivered) were **$25/ton** in 2001.
- Wood pellets
  Now $260/ton in the U.S.
  Have sold for over
  $400/ton in Europe

Wood Pellet Heater

- 16 million acres of wildfires in the U.S. in the last two years – "The new normal."
- Expect pellets to be $400/ton in the US by 2016
- Cellulosic ethanol from feedstocks at $400/ton costs over **$5.50/gal**, or $8.20/gge.

The Micro-algae Mirage

The cheapest, commercially available algae today (food industry) costs $5000/ton.

Several methods proposed for high-oil micro-algae:

(1) large plastic tanks, (2) racetrack ponds…

- Solazyme is selling non-photosynthetic algal oil to the Navy for $25-60/gal.
  - They abandoned photosynthetic algae.
  - Their CEO says it is 1000 times more expensive.
- Fuels from green algae won't be under $70/gal by 2020.

Thermonuclear-Fusion, an Impractical Dream

The latest official projections are like those of 40 years ago: "We'll see commercial, profitable, limitless electricity from fusion in about 40 years."

The *cost of the potential ITER electrical energy output would be over 10,000 times that of wind energy*.

- **The first fusion power plant, DEMO**, is projected to begin producing 500 MW net electrical output in 2035 at 50% duty cycle. (Lifetime unknown – maybe a few years.)

- **Probable initial cost (in 2012 $) of over $70/$W_{PE}$.**

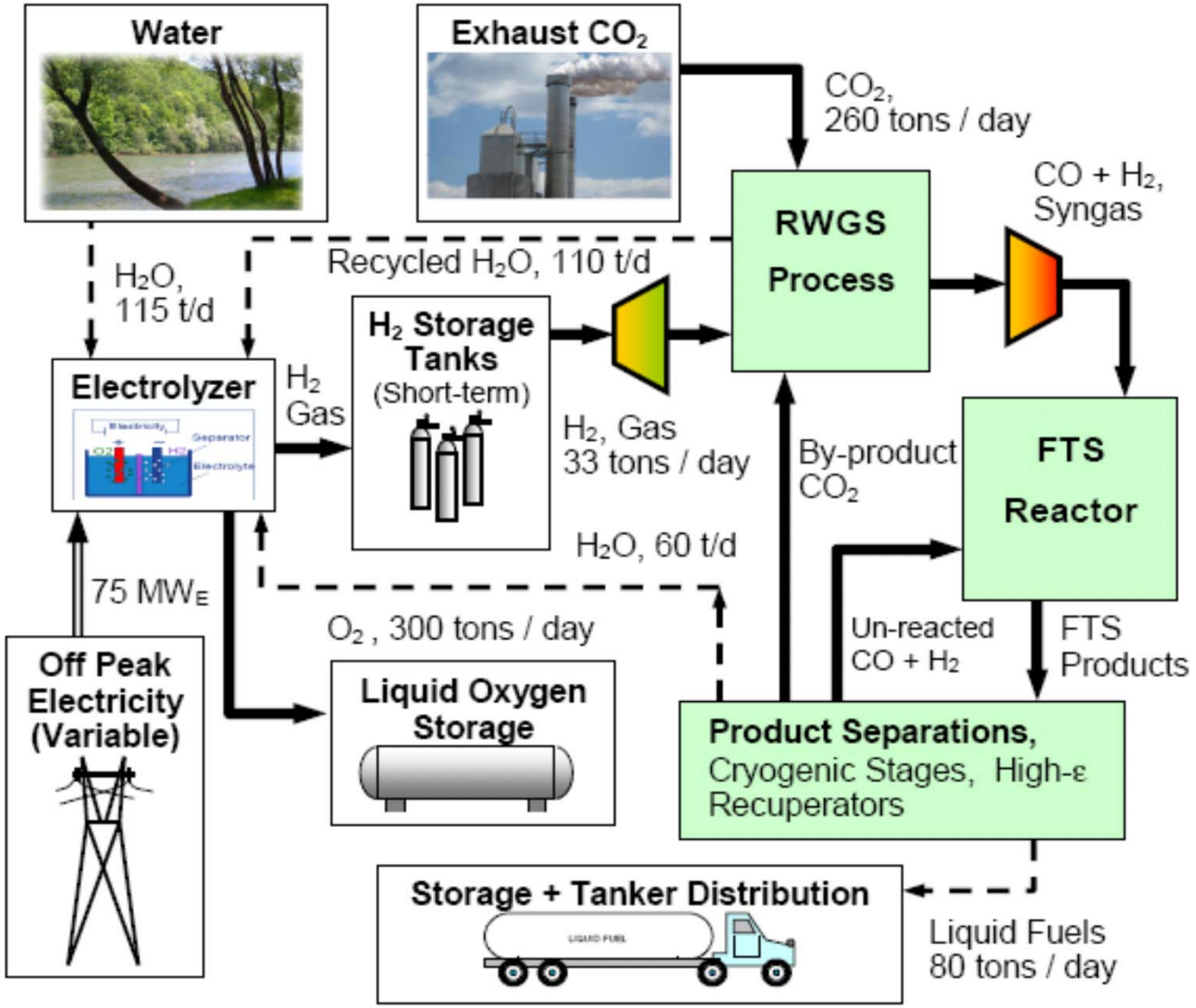
- ***If DEMO works*** as expected, its ***energy cost would be over 200 times that of wind energy***.

A Better Idea

WindFuels

Synthesizing **standard liquid fuels**
(diesel, gasoline, jet fuel…)
from CO_2 and water
using off-peak wind energy

WindFuels – Concept Overview



Build on Proven Chemistry

and improve the processes.

Start with renewable H_2 and CO from CO_2 instead of from coal.

A truly sustainable solution to the energy storage, transportation fuels, and climate challenges.

- ***There is sufficient potential excess wind energy and point-source CO_2 just in the U.S. wind corridor to make twice as much gasoline, diesel, and jet fuel as the U.S. consumes.***

Fossil-based Fischer Tropsch Synthesis

Fischer-Tropsch Synthesis (FTS), like methanol synthesis,

converts a syngas ($CO+H_2$ + some CO_2) into synfuels (diesel or gasoline) and waste heat in a catalytic reactor.

FTS reactions are not narrowly selected – i.e., they produce a wide range of products and thus require fairly complex separations.

Coal-Based Synfuels are Not Acceptable

FTS of diesel from 1 kg coal yields 2 kg of CO_2 and 0.3 kg of fuel.

RFTS (Enhanced GTL)
Renewable Fischer Tropsch Synthesis

- FTS has a long history of Commercial Application for CTL and GTL fuels
  - Germany CTL - WWII
  - South Africa - SASOL
  - Qatar – Pearl GTL (SHELL) will fuel 160,000 cars/day (<0.2% of demand)
- Process emits large amounts of CO_2

- WindFuels Plants will not be CO_2 Emitters
- RFTS will produce clean transportation fuels
- Incorporates:
  - Efficient Syngas Recycle
  - Integrated use of Waste Heat
  - Novel Recuperators
  - Produce full range of HCs
    - Most in Diesel or Jet Fuel range

The Major Technical Advances

- Nearly a **factor of two increase in the efficiency of production of syngas** from water and CO_2.
- An **order of magnitude reduction in the losses seen in recycling** of the unreacted Fischer-Tropsch (**FT**) reactants (H_2, CO_2, CO).
- Enormous **advances in cost-effectiveness of gas-to-gas recuperators** with high thermal effectiveness (up to 97%).
- Advances **in the catalysts**.
- **Optimized plant integration.**
- A **50% improvement in efficiency of conversion of waste heat** from the FT reactor and electrolyzer to electricity.

WindFuels Economics – The Basics

WindFuels can compete when oil is as low as $60/bbl.

- At $15/MWhr, the wind energy cost in jet fuel or gasoline will be $1.00/gal – and for ethanol, about $0.68/gal.
- The CO_2 ($40/ton) might initially cost ~$0.40 per gallon of product, but eventually it will be nearly free.
- The co-produced (nearly free) liquid oxygen (LOX) may be worth up to $1 per gallon of liquid fuels produced.
- Pay-back on the RFTS plants will usually be under 3 years.
- Mid-term assumptions: mean wind energy cost of $4.2/GJ ($15/MWhr); electrolysis HHV efficiency of 75%; RFTS plant efficiency of 75% HHV; 55% net system HHV efficiency.

Fischer-Tropsch Chemistry

In most GTL plants, the syngas comes from natural gas, mostly via the following endothermic steam reforming reaction:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \quad , \quad \Delta H = 218 \text{ kJ/mol} \qquad [1]$$

and the so-called water gas shift (WGS),

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad , \quad \Delta H = -38.9 \text{ kJ/mol.} \qquad [2]$$

The CO and H_2 are converted to fuels and water, such as octane, on the surface of catalysts at suitable conditions,

$$8CO + 17H_2 \rightarrow C_8H_{18} + 8H_2O \quad , \quad \Delta H = -1282 \text{ kJ/mol.} \qquad [3]$$

The yield for mid-alcohols in most FTS has been extremely low, but ethanol selectivity above 25% has been achieved with several recent catalysts, including K_2CO_3-promoted β-Mo_2C and K/Zr/Zn/Mn. For ethanol, the net reaction is

$$2CO + 4H_2 \rightarrow C_2H_5OH + H_2O \quad , \quad \Delta H = -272 \text{ kJ/mol} \qquad [4]$$

The theoretical efficiency limit for ethanol production from H_2 and CO_2 can be shown to be ~90%. 58% is a reasonable goal.

Practical, Renewable CO Required

The Reverse Water Gas Shift (RWGS)

The water-gas-shift (**WGS**) reaction is widely used in commercial processes for production of H_2.

However, the **RWGS** reaction, shown below, has not yet been practical for reduction of CO_2 to CO.

$CO_2 + H_2 \rightleftarrows CO + H_2O$, $\Delta H = 38.9$ kJ/mol

The equilibrium constant K_P is defined by

$$K_P = \frac{p_{H2O}\ p_{CO}}{p_{CO2}\ p_{H2}}$$

where the *p*'s are the partial pressures.

More on Scale-up – the Big Picture

1st : Wind-Turbine Manufacturing

• At least ten multi-billion-dollar companies around the world build and install multi-megawatt wind turbines.

2nd : The Water Electrolyzer

• This may represent up to 35% of the capital for expected near-term electrolyzer prices.

3rd : The RFTS Plant

• Much of the equipment is produced for GTL plants.

4th : CO_2 separation processes at existing plants

The high cost of electrolyzers for the next 5-8 years represents the only real challenge for Windfuels.

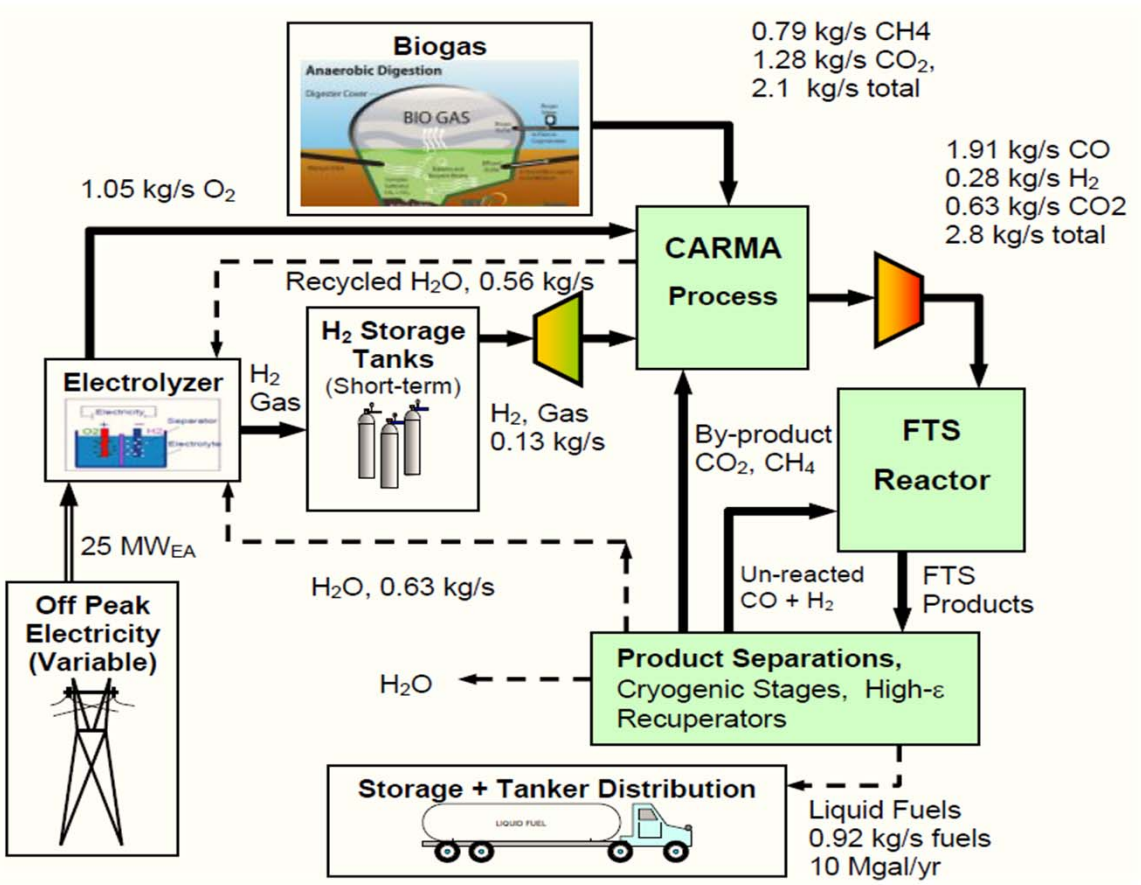
CARMA – A Lower-Cost Bridging Solution

(**C**O_2 **A**dvanced **R**eforming of **M**ethane **A**diabatically)

Synergistically combine biogas or shale gas with off-peak wind.

Reduce electrolyzer and wind-energy needs by a factor of 3 to 10.

Begin driving the electrolyzer industry to the scale needed for Windfuels.



Fuel costs from $0.85/gal to $2.50/gal.

SYNGAS PRODUCTION

RWGS

- CO_2 from point source emitters
  - Cleaned to high purity
    - Simple, Low $ process
- Primary Reaction
  - RWGS $CO_2 + H_2 \rightarrow CO + H_2O$
  - Reverse of more common commercial WGS reaction
- Proprietary Catalyst
  - 20-100X CO productivity compared to other published catalysts

CARMA

- Leads to Better near-term ROI from reduced electrolyzer demands and less Hydrogen Storage needs
- Methane and CO_2 from:
  - Shale Gas, Bio Gas, or Wood Gas
- CARMA Reactions
  - RWGS $CO_2 + H_2 \rightarrow CO + H_2O$
  - Dry reform $CH_4 + CO_2 \rightarrow 2CO + 2H_2$
  - SMR $CH_4 + H_2O \rightarrow CO + 3H_2$
  - De-coking $C + H_2O \rightarrow CO + H_2$
  - CH_4 oxid $CH_4 + 2O_2 \rightarrow CO_2 + H_2O$

Product Separations

- Products from RFTS reactor will include Full Range of Hydrocarbons, mostly n-Alkanes and Alkenes.
- Cryogenic and Flash separations to Increase Efficiency even at Low Throughput
- Store for Distribution or Further Refine

- Novel Packed-Column and Phase-Separator Designs
- Modern, Advanced Controls
- Dramatically Reduced Need for Custom Engineering
- Primary Straight-run Products:
  - Blending Stocks for Gasoline, Jet Fuel, Diesel, and Lubricants
  - High-purity Olefin Feedstocks for "Green" Plastics
  - Liquid Oxygen (from WindFuels)

Stabilizing the Grid to 50% Wind

- The electrolyzer can respond in milliseconds – so the WindFuels plant will draw electrical power to produce (and store) hydrogen only during off-peak hours.
- The chemical processes will run more steadily, but they can be ramped up and down in a few hours.
- WindFuels solves both short-term energy storage (in hydrogen) and long-term energy storage (in liquid fuels.)
- WindFuels will allow wind energy to grow from the current 2.5% to over 50% of the grid.

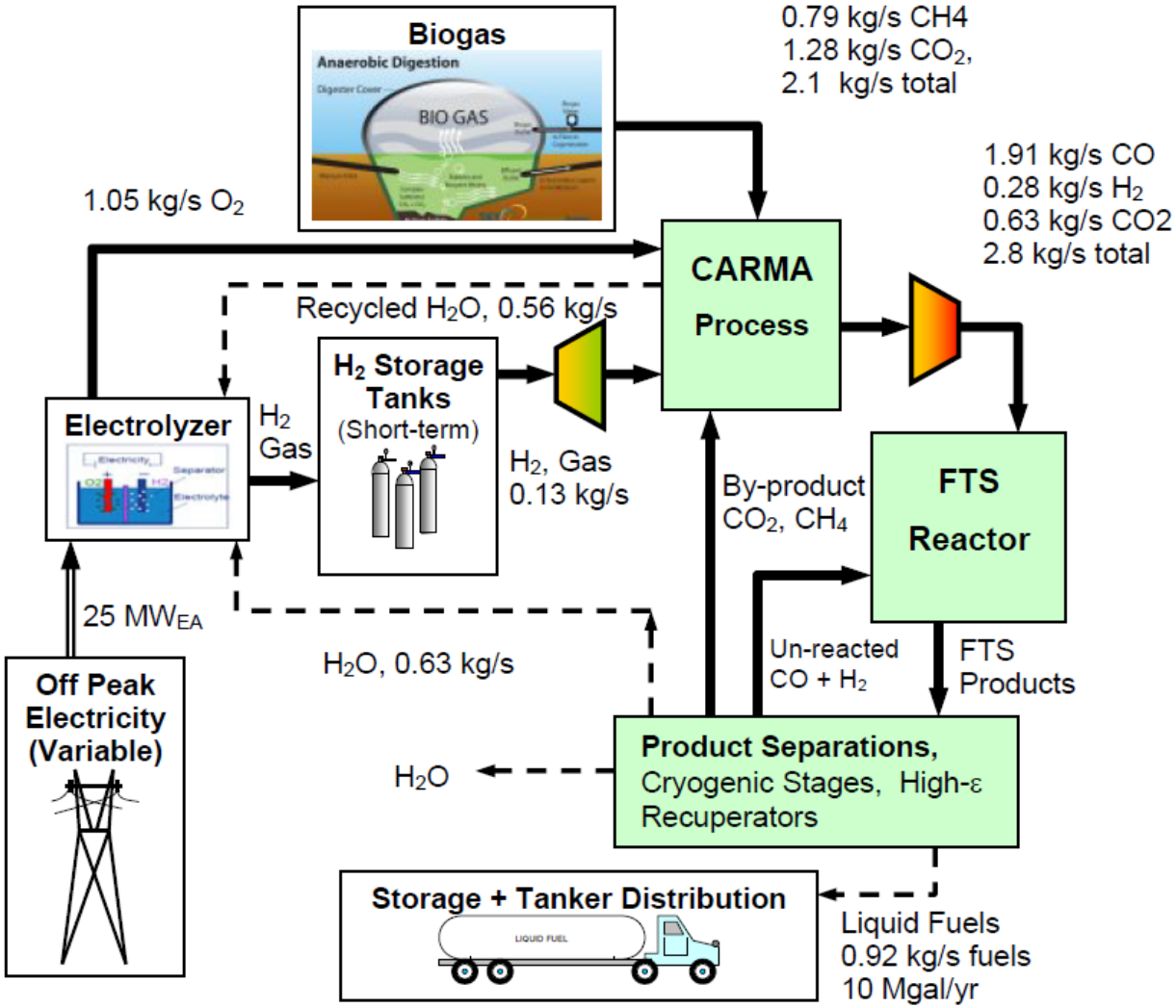
There is enough potential, recoverable wind energy to make more than twice as much fuel as we currently use in transportation.

Efficiency is actually not the biggest issue…

It's the price of off-peak grid energy and the price of oil that matter the most.

- **The price of off-peak grid energy today is *half* what it was four years ago in many areas of high wind penetration.**
- **We're still only at 10% wind energy in the best states.**
- ***Will we see 5 hours of free, clean, grid power most nights in the wind corridor 8 years from now?***
- **Probably – unless we begin investing heavily (and soon) in CARMA and WindFuels.**

WindFuels / CARMA Recap



Driving the wind market – to 20% well before 2024

Doty Energy

WindFuels

- The RWGS and CARMA reactions can be utilized to produce the needed syngas (CO and H_2) at efficiencies approaching theoretical limits.

- With well optimized processes, we can sustainably synthesize everything we currently get from petroleum at prices that compete with oil.

- We'll be able to do this soon enough to avoid an oil price surge that would have dire global consequences.

Thank you for your attention !