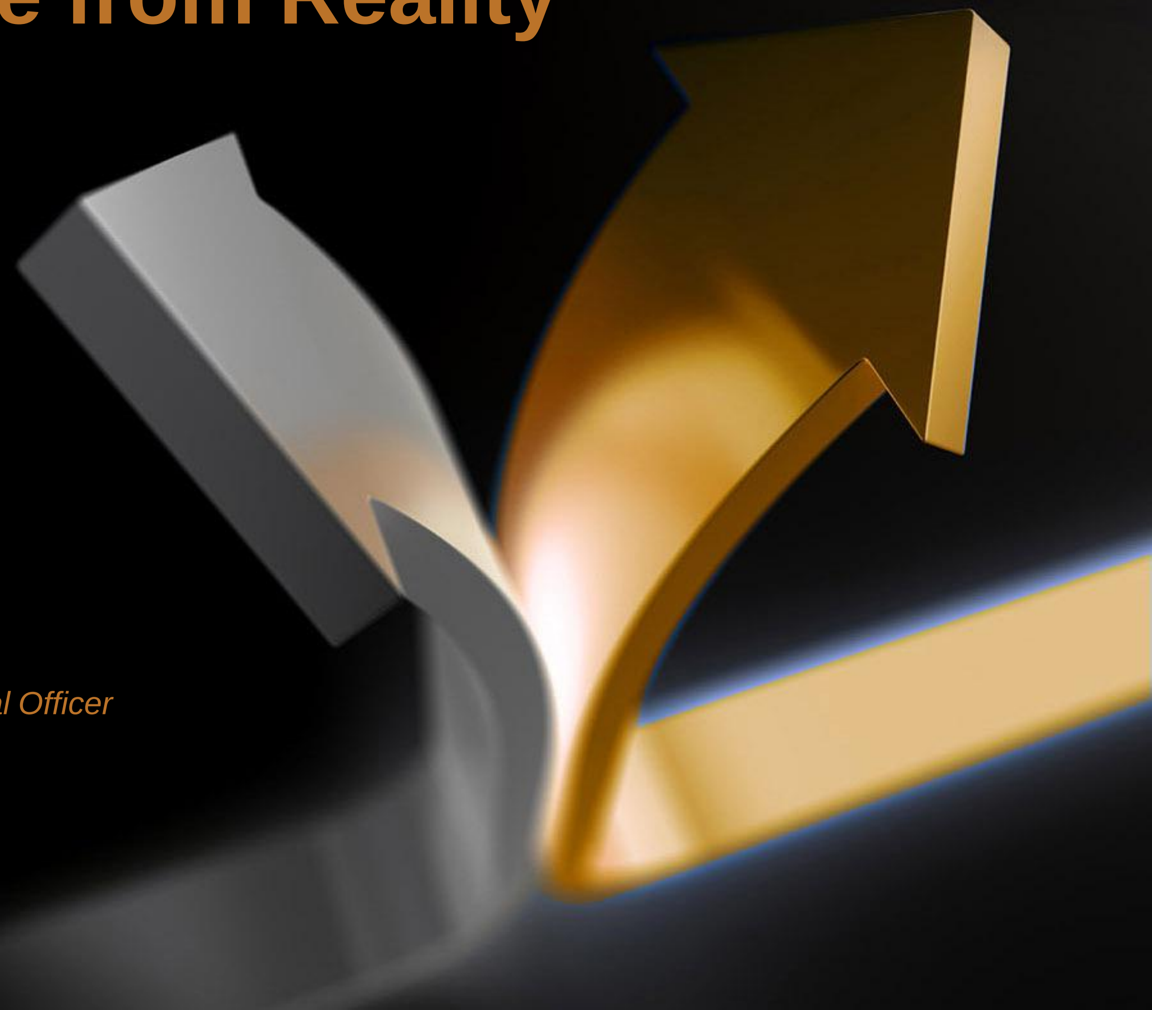
Quinn Lecture
University of Pennsylvania
27 March 2013

Materials Solving Energy Issues: Separating Hype from Reality



William F. Banholzer
Executive Vice President and Chief Technical Officer
The Dow Chemical Company

Call to Scientists and Engineers

"Too much hype for the possible and not enough on focus on the practical.

We are letting society down!"

Hype Around Cleantech

Ivy League Brains Figure Out How to Make Biodegradable Plastic from Greenhouse Gases

September 28, 2012 cleantechnica.com

Two graduates from Princeton University and Northwestern University have developed a process for converting greenhouse gases from sewage treatment plants, landfills, and power plants into a biodegradable plastic called Airflex™

As described by Newlight, the process for making Airflex ™ breaks down into a few simple steps. First, a mix of gases, including methane and carbon dioxide, is funneled into a reactor. Next, carbon and oxygen are separated out, and then they are reassembled into a long-chain thermopolymer.

September 25, 2012 presswire.com

"We are pleased to receive this seventh patent," stated Newlight CEO, Mark Herrema . "While the size of our patent portfolio is a testament to Newlight's pioneering inventions and nearly decade-long leadership in this field, we expect our patent portfolio to continue to grow at a rapid pace, particularly in the areas of new product applications and commercial-scale manufacturing systems."

Permanent Exhalation Conveyance

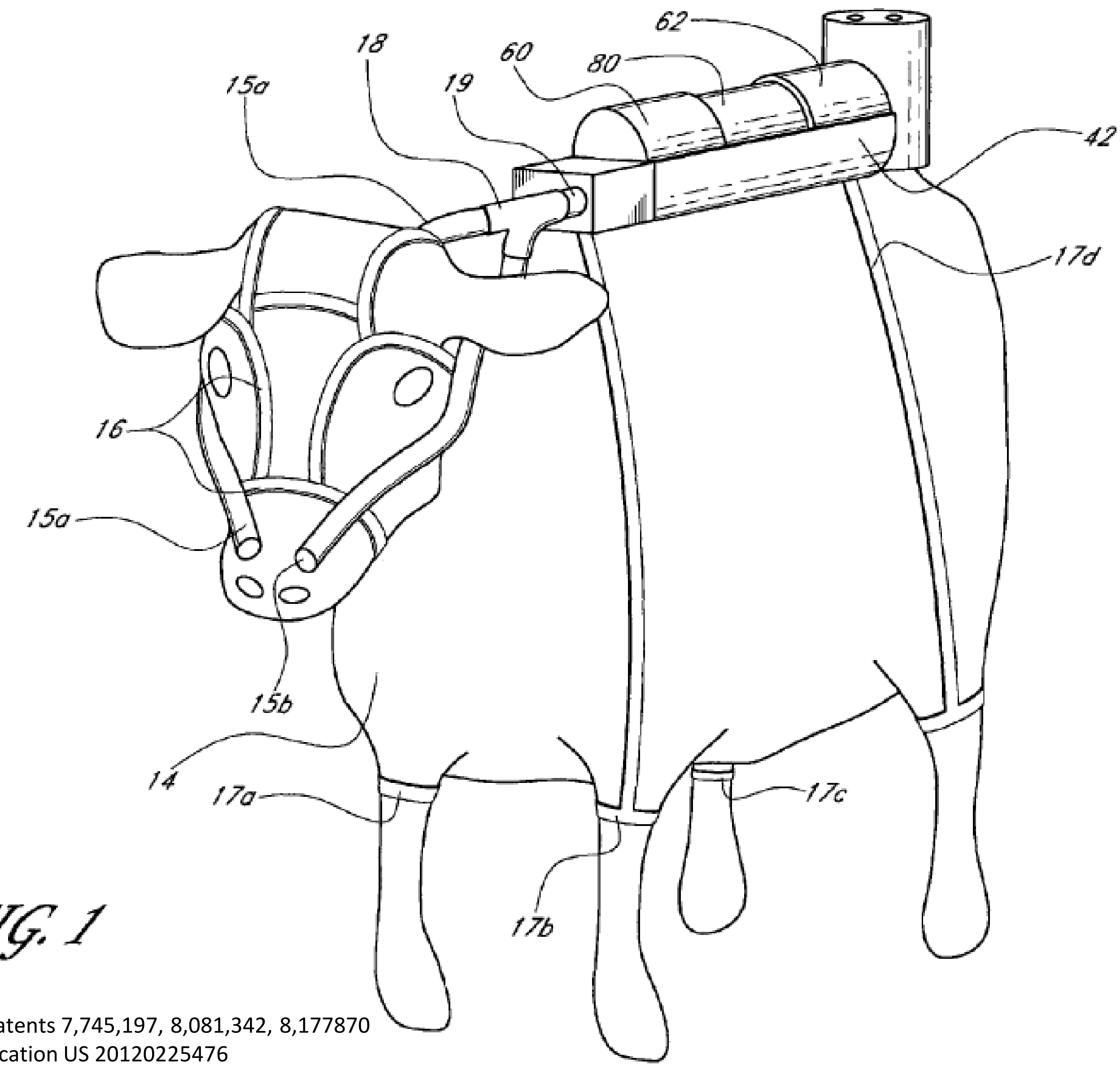
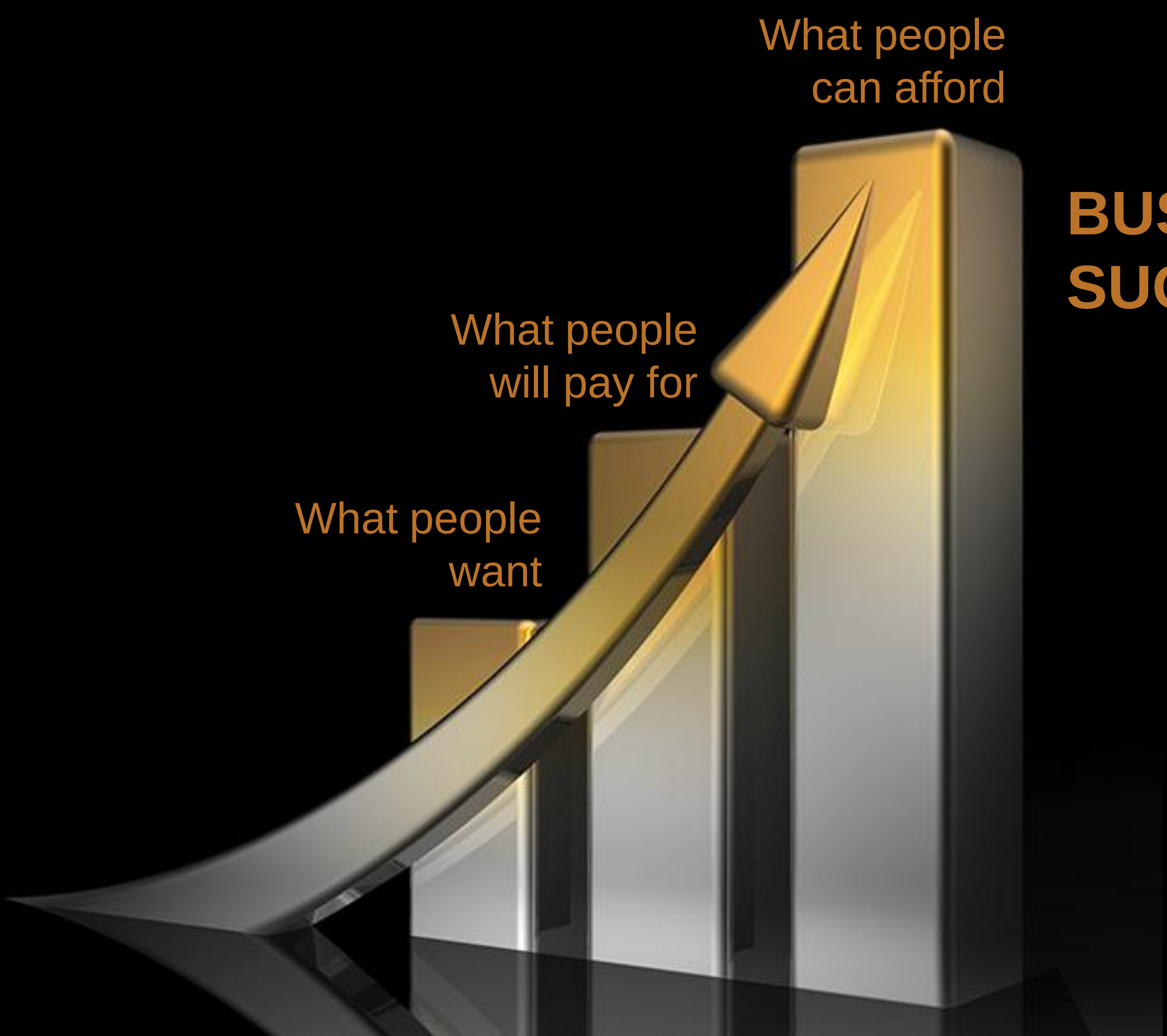


FIG. 1

US patents 7,745,197, 8,081,342, 8,177870
application US 20120225476

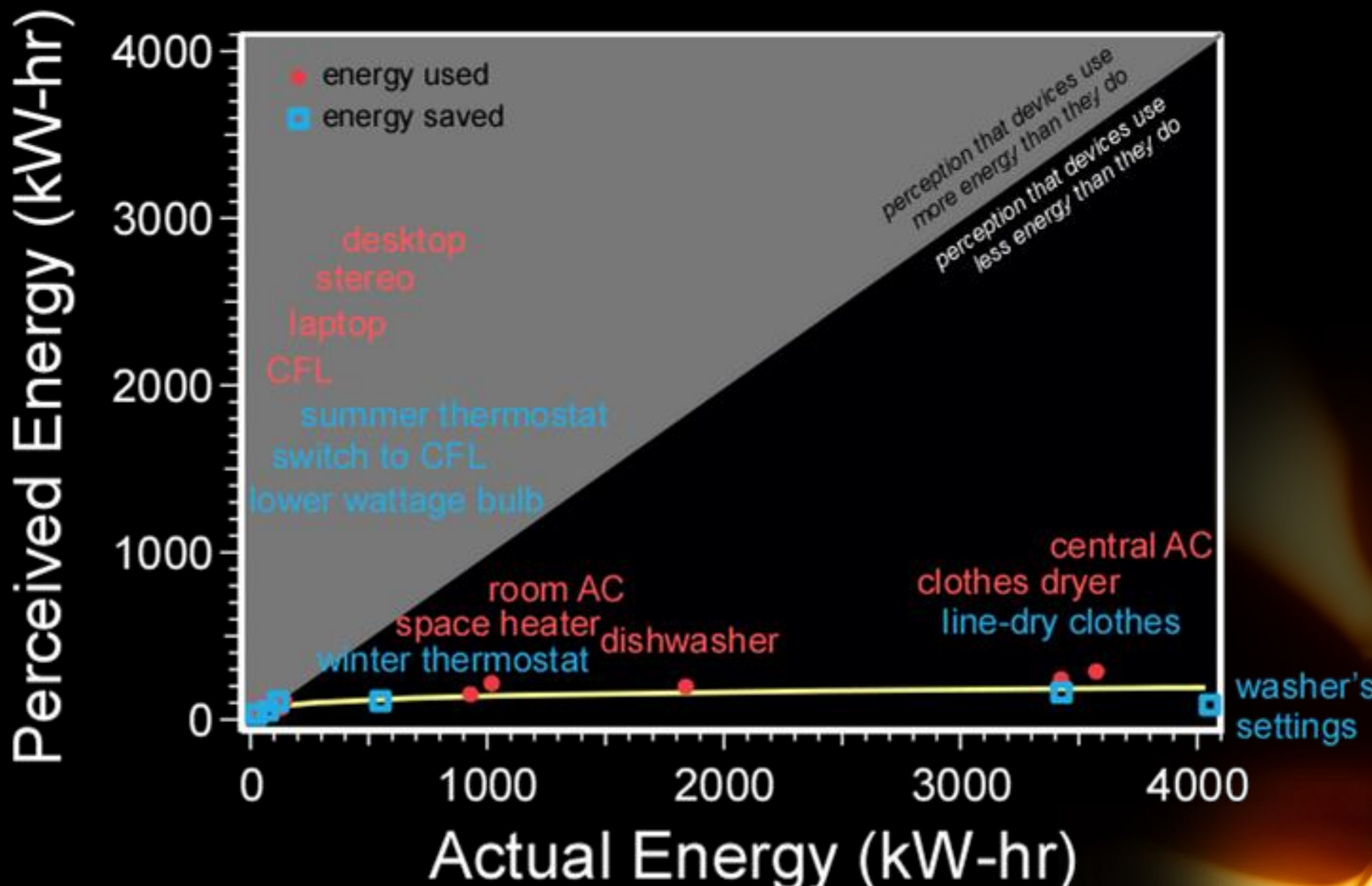
Rules for Business

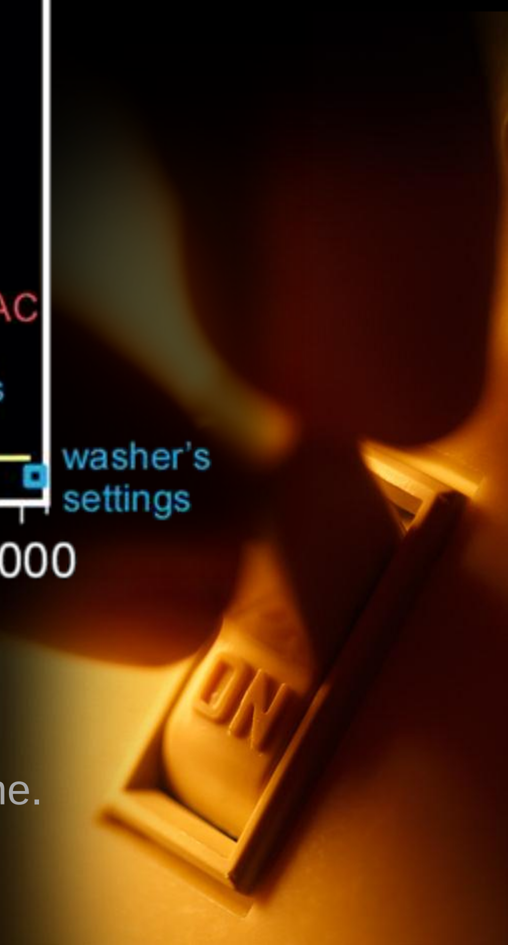


BUSINESS SUCCESS

We Are Poor Judges of the Energy We Use

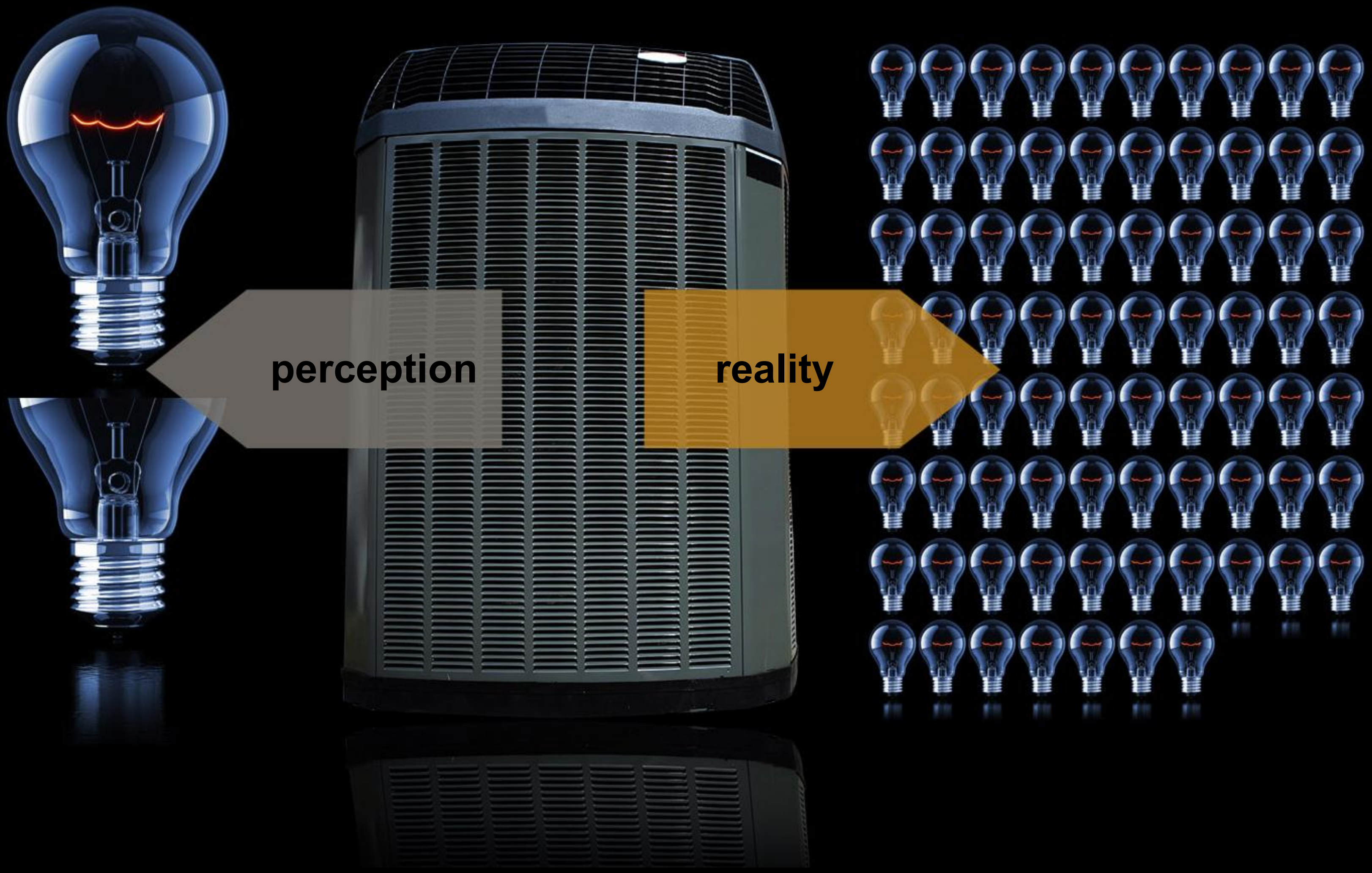
DOW



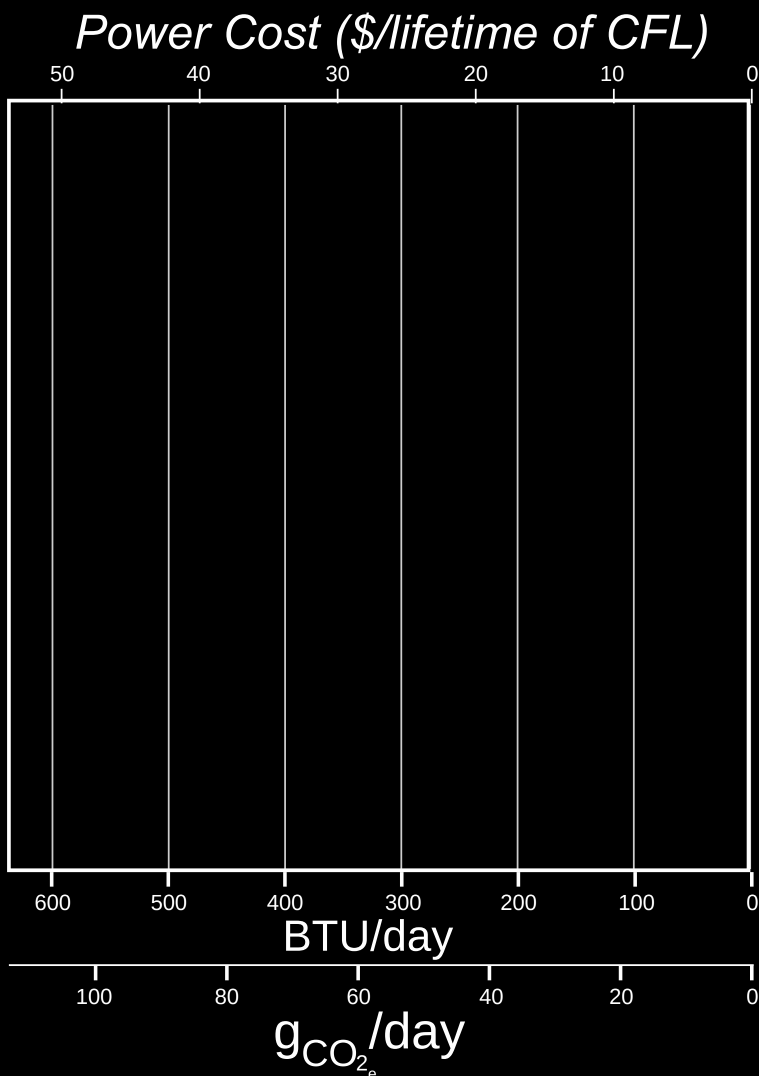


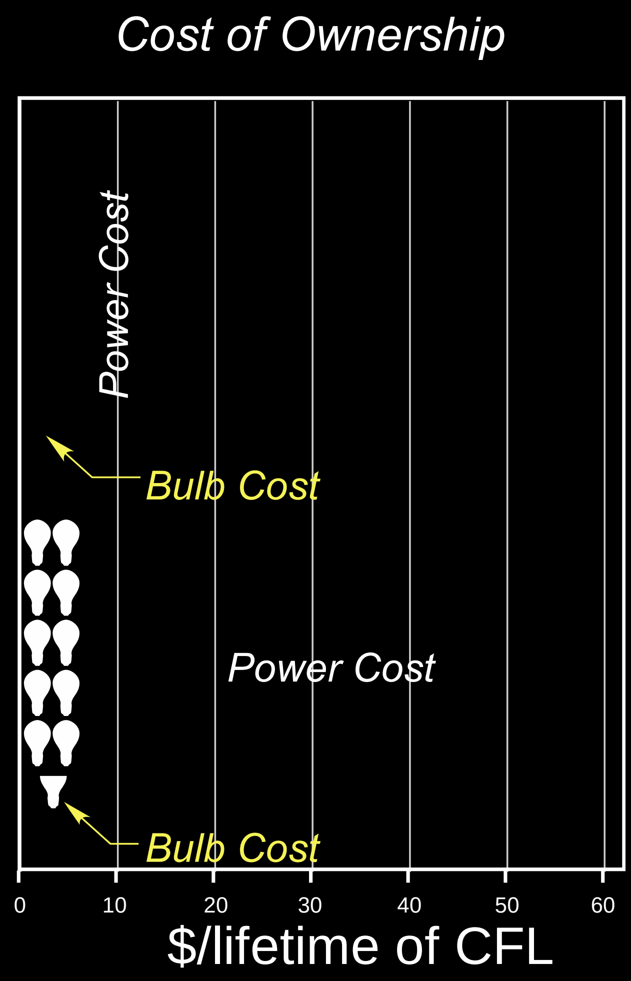
We are poor judges of how much energy everyday devices consume.

Energy Perception and Reality

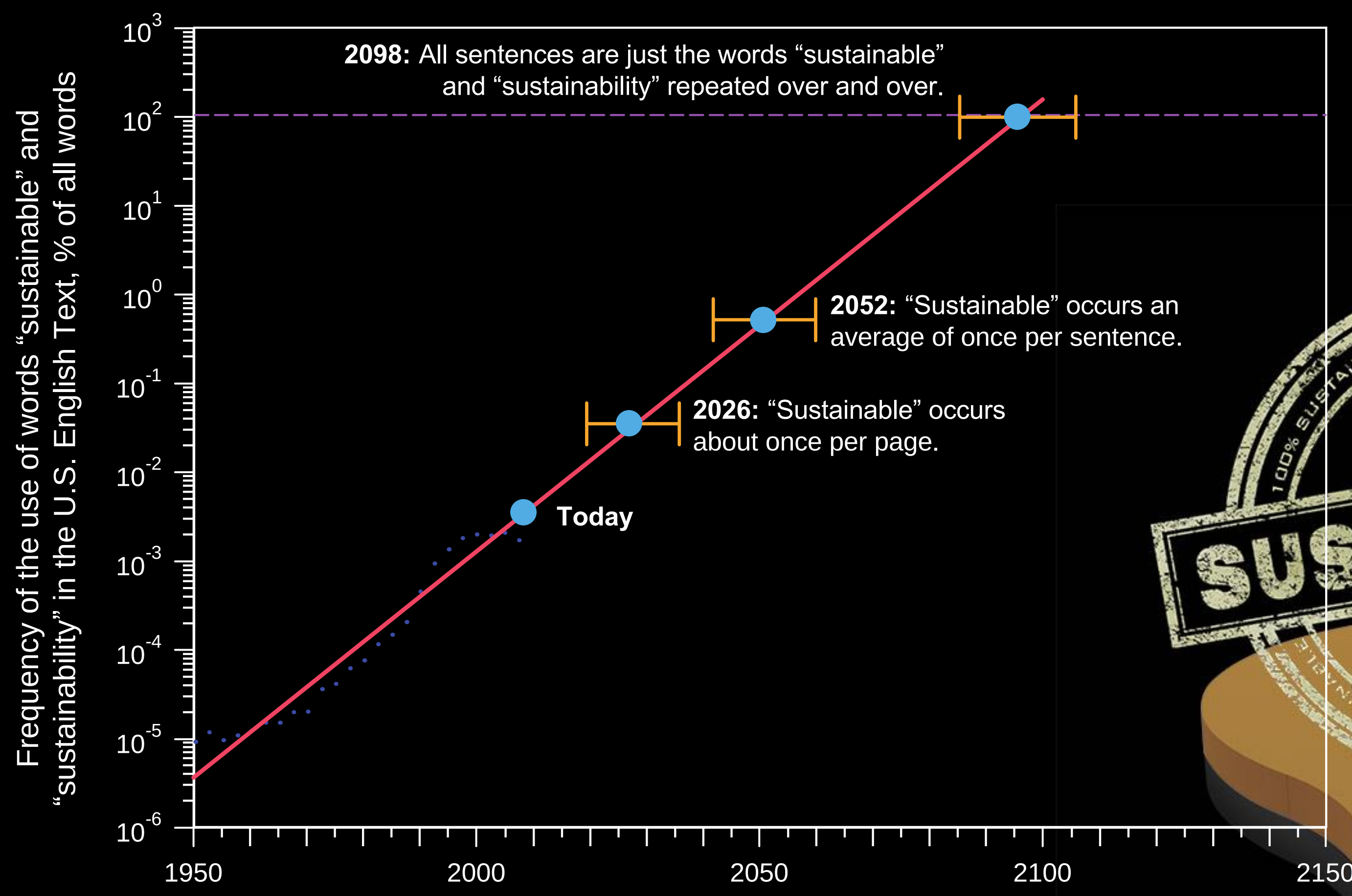


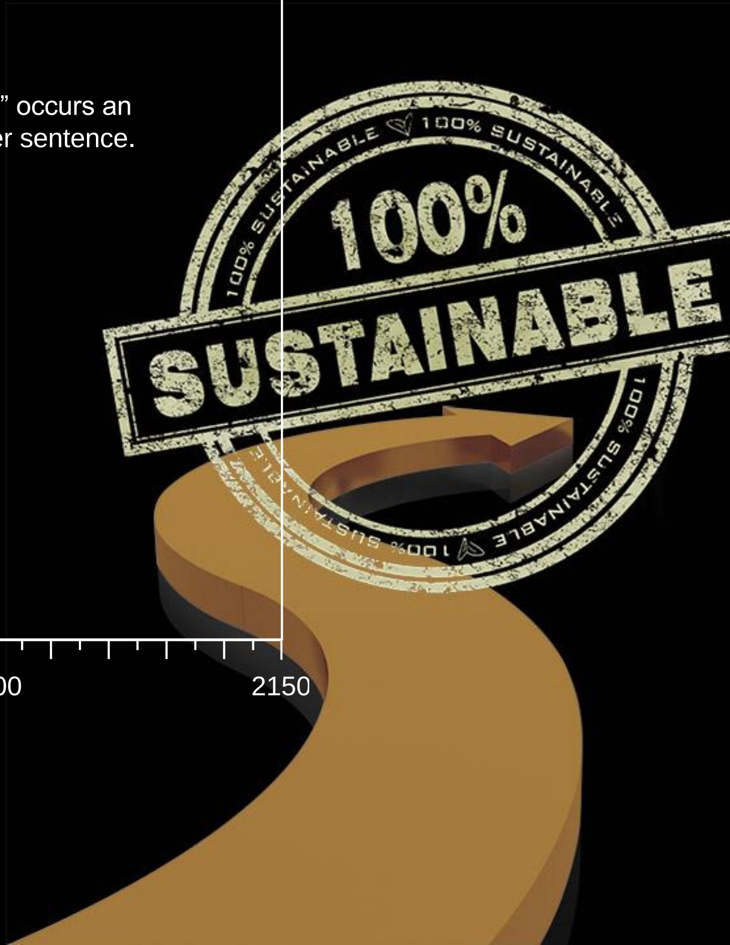
People Don’t Always Make Smart Choices





Ripe for Hype





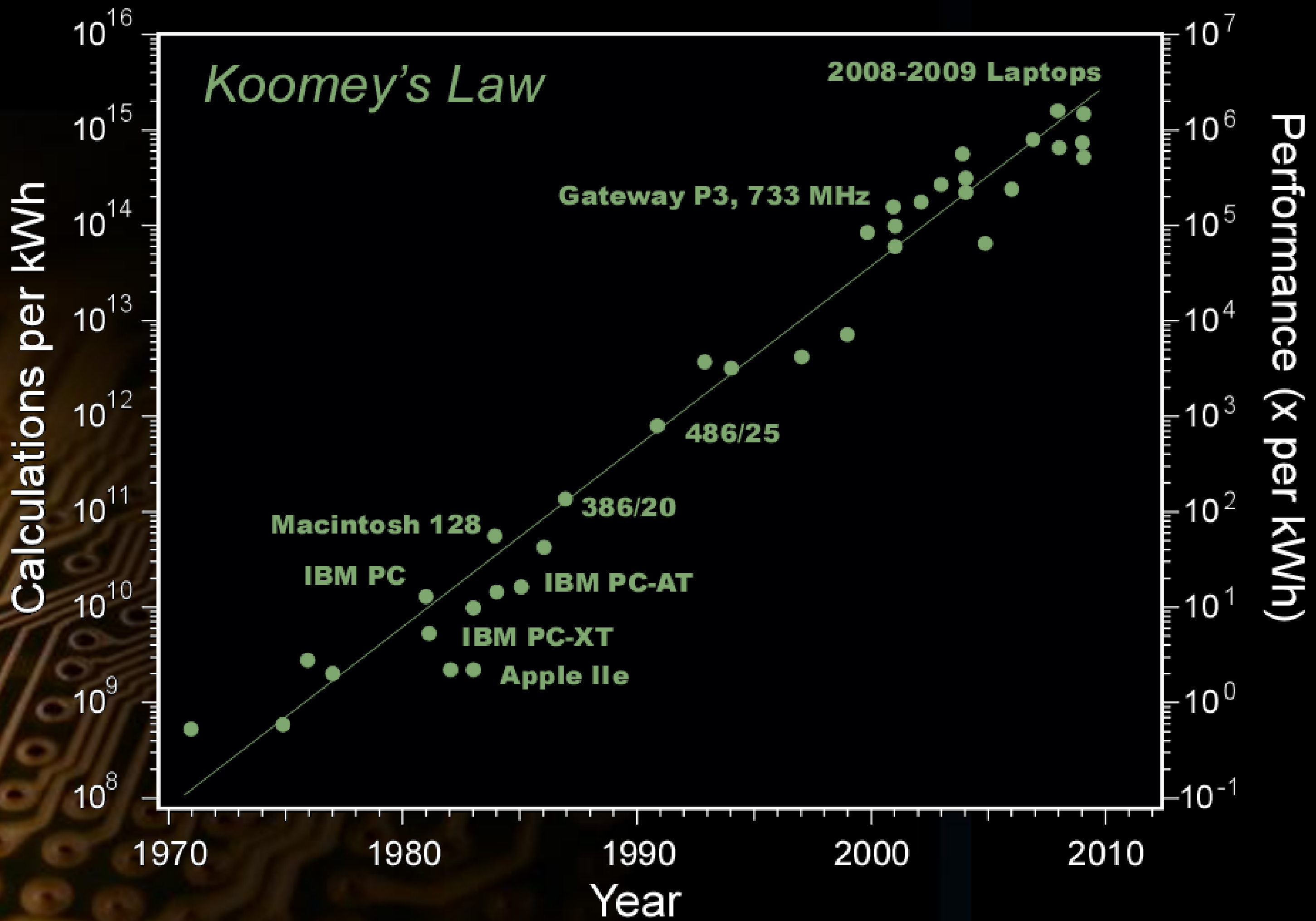
Source: Google Ngrams

Gross Mismatch

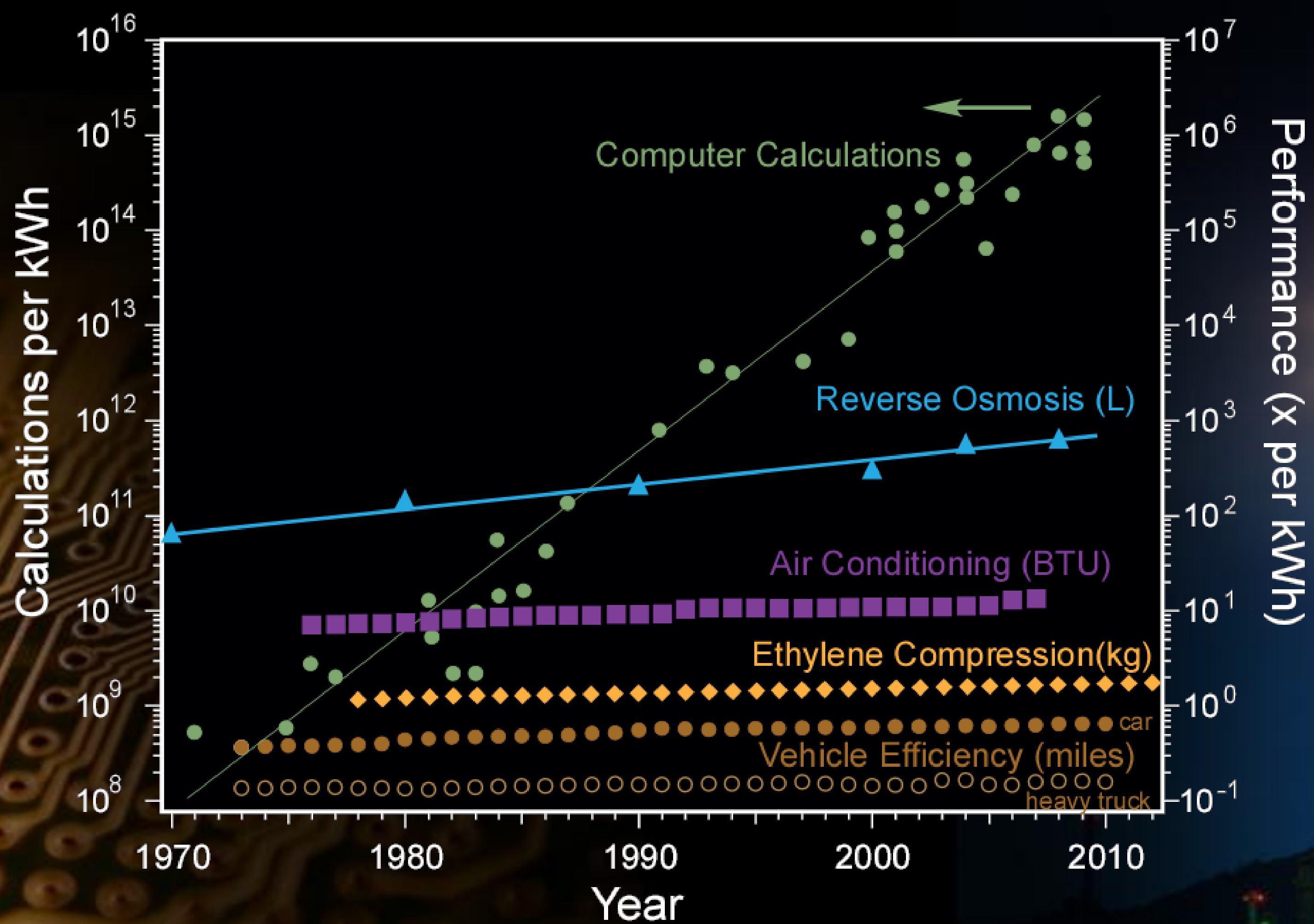
Expectations are sky high.

Understanding is low.

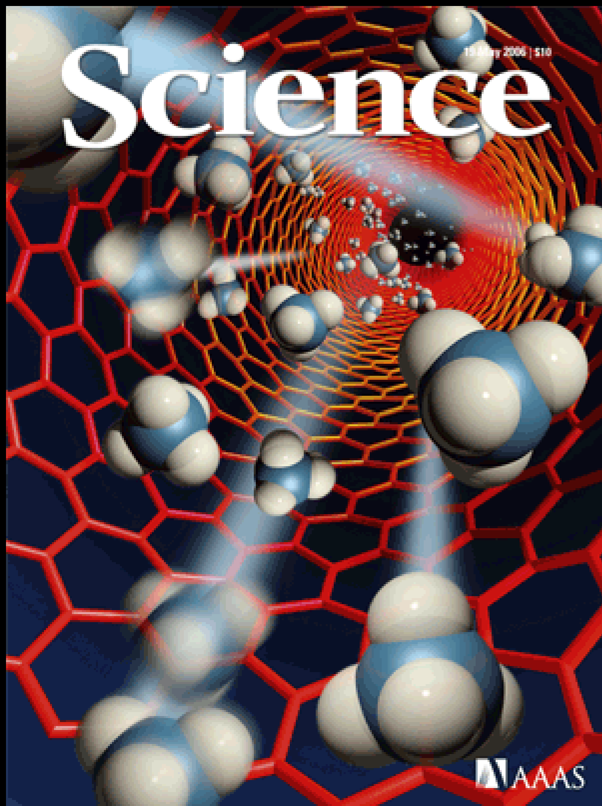
Engineering Triumph



Moore's Law Sets Unrealistic Expectations



Nanotubes for Desalination



Fast Mass Transport Through Sub–2-Nanometer Carbon Nanotubes

Jason K. Holt,[1*] Hyung Gyu Park,[1,2*] Yinmin Wang,[1] Michael Stadermann,[1] Alexander B. Artyukhin,[1] Costas P. Grigoropoulos,[2] Aleksandr Noy,[1] Olgica Bakajin[1]†

We report gas and water flow measurements through microfabricated membranes in which aligned carbon nanotubes with diameters of less than 2 nanometers serve as pores. The measured gas flow exceeds predictions of the Knudsen diffusion model by more than an order of magnitude. The measured water flow exceeds values calculated from continuum hydrodynamics models by more than three orders of magnitude and is comparable to flow rates extrapolated from molecular dynamics simulations. The gas and water permeabilities of these nanotube-based membranes are several orders of magnitude higher than those of commercial polycarbonate membranes, despite having pore sizes an order of magnitude smaller. These membranes enable fundamental studies of mass transport in confined environments, as well as more energy-efficient nanoscale filtration.

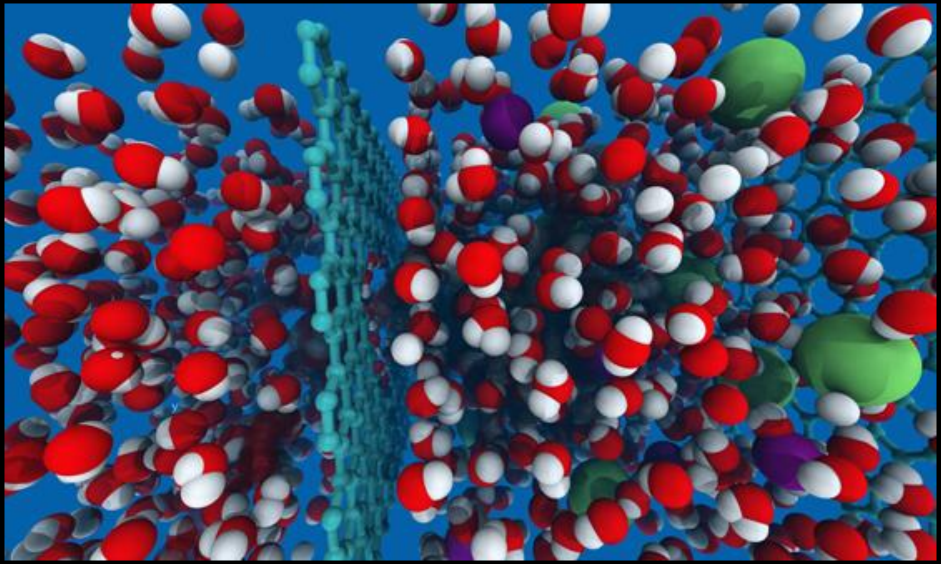
"NanOasis proposes to utilize carbon nanotubes (CNTs) to make industrially-scalable reverse osmosis (RO) membranes ….We target a ten-fold permeability increase compared to today's commercial state-of-the-art, resulting in a 30-50% energy savings…"

Graphene for Desalination Membranes

Pentagon weapons-maker finds method for cheap, clean water

By David Alexander

WASHINGTON | Wed Mar 13, 2013 1:15am EDT



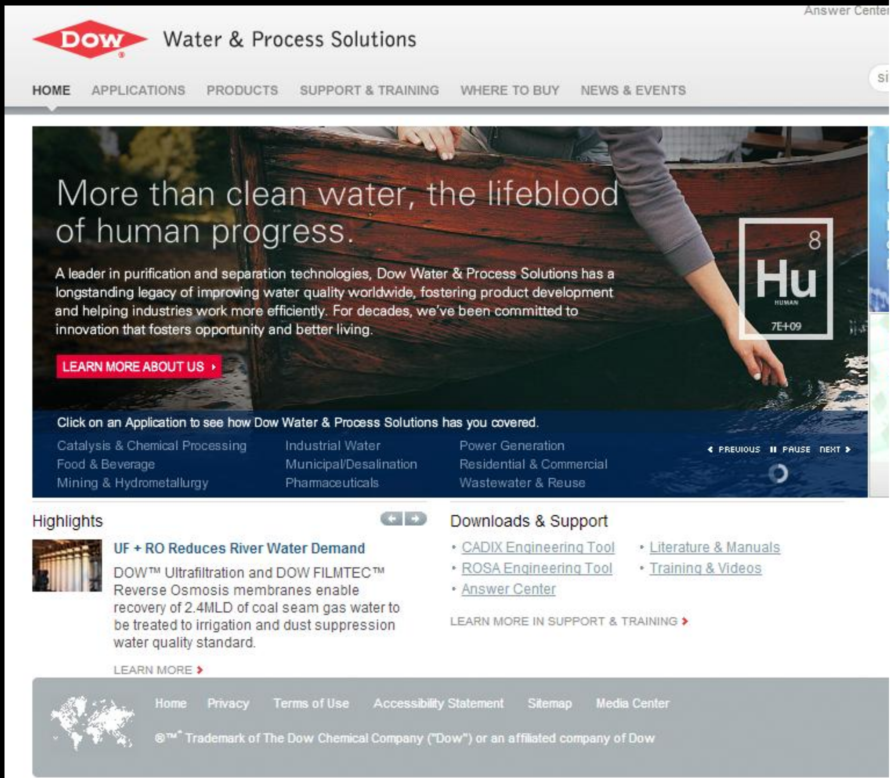
WASHINGTON (Reuters) - A defense contractor better known for building jet fighters and lethal missiles says it has found a way to slash the amount of energy needed to remove salt from seawater.....

Because the sheets of pure carbon known as graphene are so thin - just one atom in thickness - it takes much less energy to push the seawater through the filter with the force required to separate the salt from the water, they said.

The development could spare underdeveloped countries from having to build exotic, expensive pumping stations needed in plants that use a desalination process called reverse osmosis.

"It's 500 times thinner than the best filter on the market today and a thousand times stronger," said John Stetson, the engineer who has been working on the idea. "The energy that's required and the pressure that's required to filter salt is approximately 100 times less."

What Would You Do?



Dow Water and Process Solutions

World-Class Solutions. Worldwide Impact.

The global leader in sustainable separation and purification technology, **Dow Water and Process Solutions** is making a clear impact in every corner of the globe – from developing countries to the most advanced industrialized nations. Building on its 50-year legacy of providing innovative water and process solutions to consumers, communities, municipalities and industries alike, Dow Water and Process Solutions is spearheading the development of sustainable technologies that integrate water and energy requirements. Today, its technologies are helping to make water safer and more accessible, food taste better, pharmaceuticals more effective and industries more efficient. In addition to being one of the world's largest manufacturers of reverse osmosis water purification membranes, the business also is a leading provider of a broad portfolio of ion exchange resins, ultrafiltration membranes and electrodeionization products.

ELEMENTS OF MARKET SUCCESS

- #1 position in reverse osmosis and ion exchange resin technologies
- Only manufacturer to offer a complete portfolio of advanced water treatment technologies
- Advances in technology have significantly reduced the cost of water by lowering our customers' energy consumption by as much as 50 percent over the past 15 years
- Expanded manufacturing and R&D footprint increases service levels to regional customers, strengthening global competitiveness
- Positioned to address rapidly rising demand for safer water, energy and food supplies due to an increasing global population and urbanization

MARKET GROWTH OPPORTUNITIES

- By 2015, 5 billion people will live in areas of significant water stress. Dow Water & Process Solutions' addressable market is projected to double by 2020.

Today (in billions): Dow ~$1; Addressable market >$5

By 2020 (in billions): Dow ~$3.5; Addressable market >$10

RECENT STRATEGIC ACHIEVEMENTS

- July 2011: Announced construction of a new reverse osmosis manufacturing facility in Saudi Arabia to enable the production of drinking water from seawater
- June 2011: Opened a Desalination Technology Development Center in Tarragona, Spain
- 2009–2011: Expanded R&D capabilities in India and Brazil and announced collaboration with the King Abdullah University of Science and Technology on water treatment technologies at the Dow R&D Center in Saudi Arabia

KEY INSTALLATIONS FOR DOW MEMBRANES

- Soreq, Israel – Membranes used in the world's largest desalination plant, currently under construction
- Ashkelon, Israel – Provide up to 15 percent of Israel's clean water
- Perth, Australia – Largest desalination facility in the Southern Hemisphere, treat 144,000 m³ of seawater per day
- Florida, United States – Produce 25 million gallons of safe water per day at largest desalination plant in the United States
- Shoaiba, Saudi Arabia – One of Saudi Arabia's largest reverse osmosis seawater desalination plants

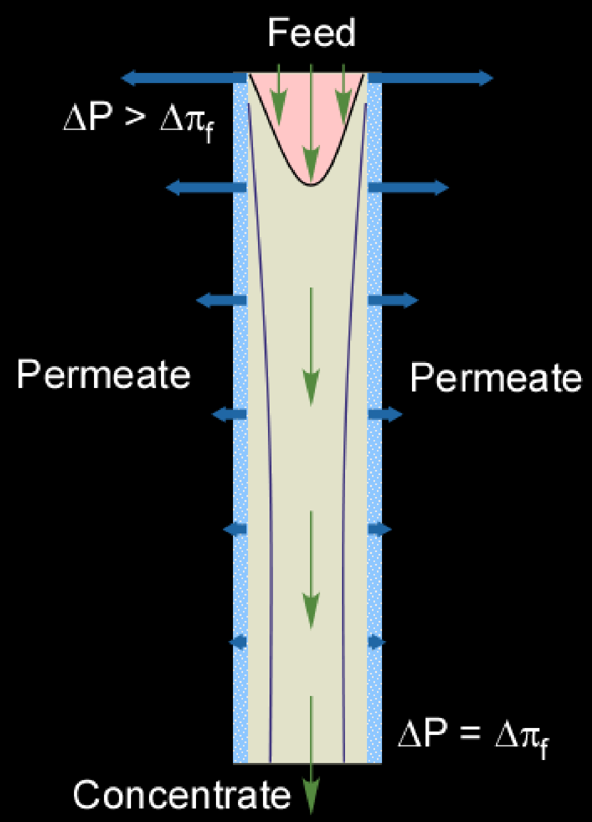
The Dow Chemical Company

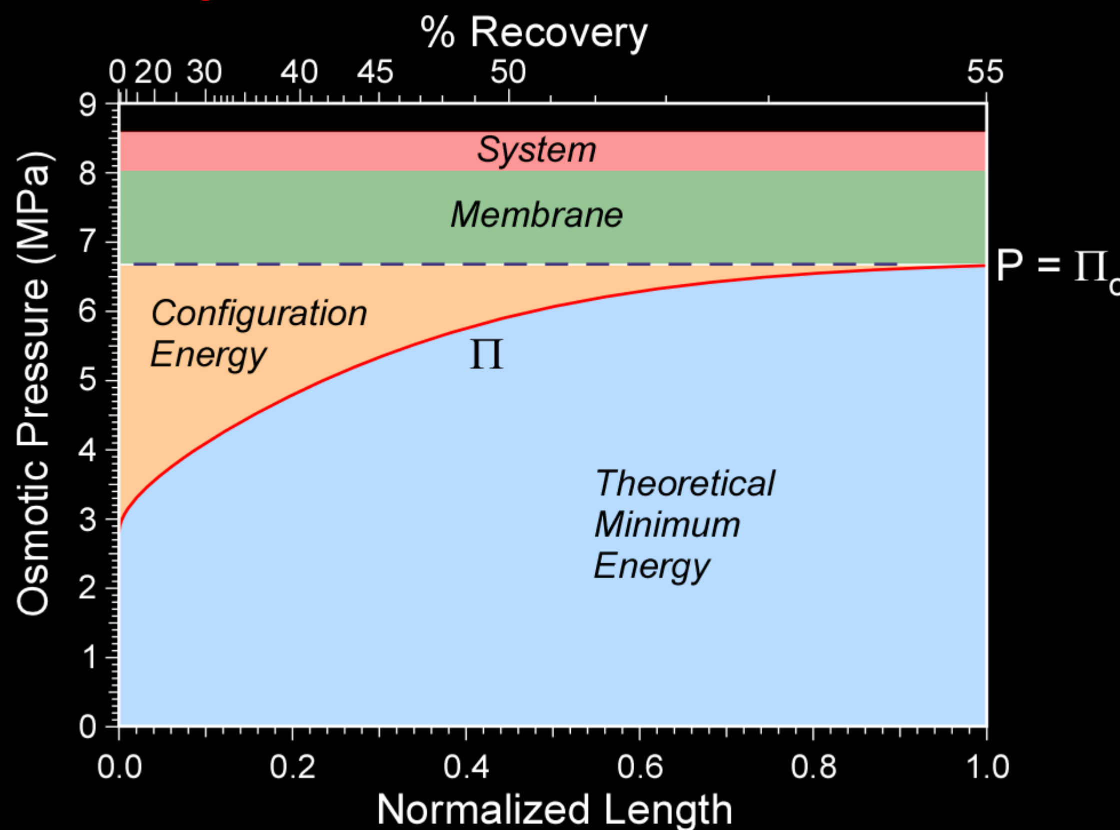
What are key technical questions you would ask at CTO of Dow?

Thermodynamics

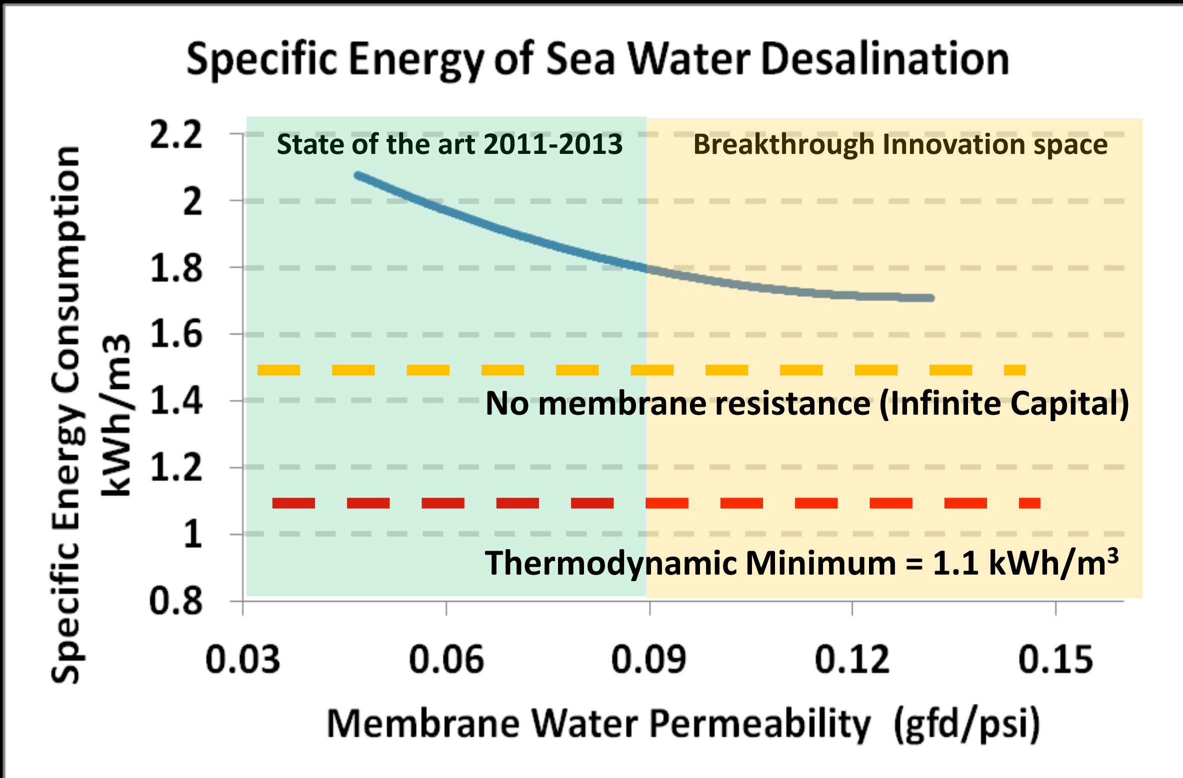
$$-d(\Delta G_{mix}) = -RT\ln a_w \, dn_w$$
$$= \prod\nolimits_s \vec{V}_w \, dn_w$$

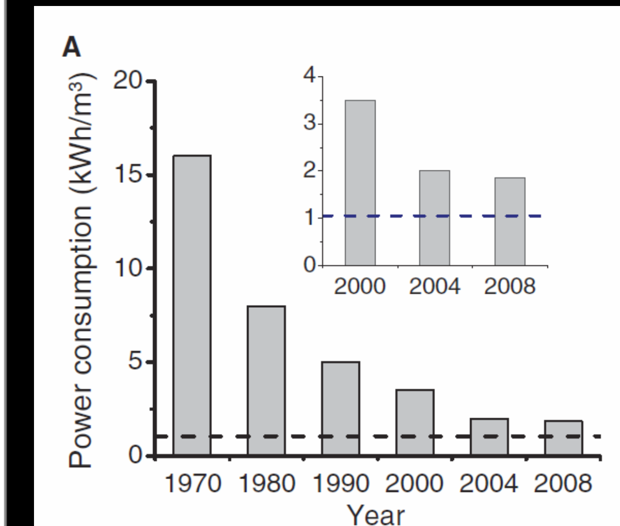
Real World





Membrane Improvements





Thermal Desalination ~8-15 kWhr/m^3

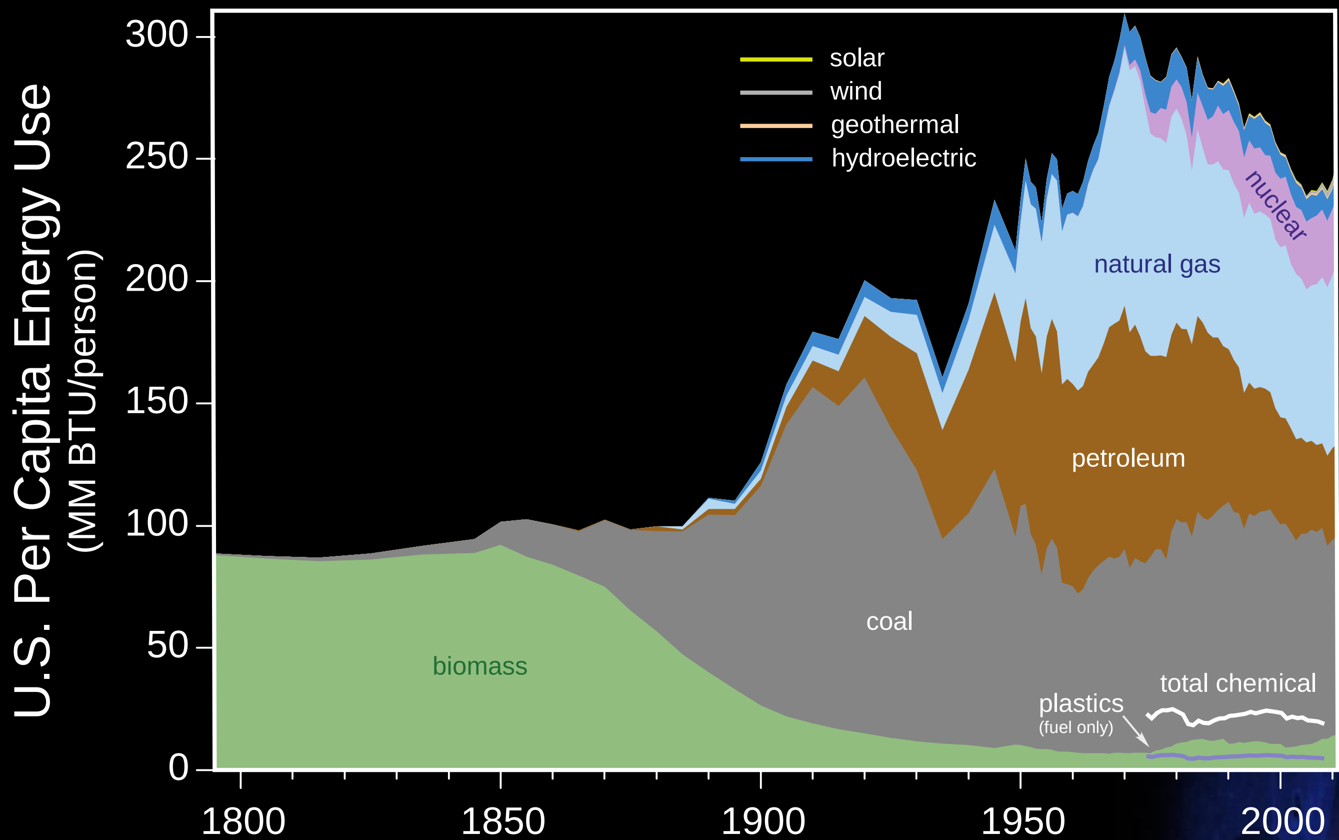
Current RO Energy Efficiency ~2 kWhr/m^3

Theoretical Minimum Energy= 1.1 kWh/m^3 (50% Recovery 3.5% salt)

Ideal, Single Stage Energy Efficiency =1.56 kWh/m^3

Elimelech et al., Science 333, Aug 2011
Miller, Sandia report 2003; Elimelech JMS 2003.

Energy Sources Always Change



What's changed?

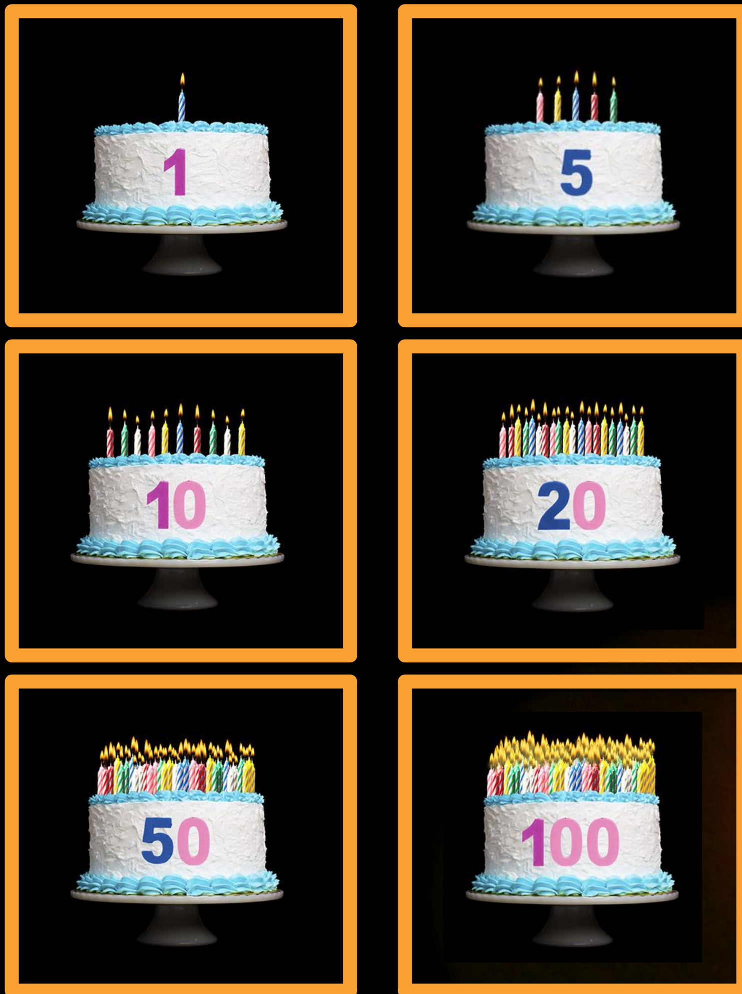
- Oil price rise
- CO_2 awareness

Will this reverse the trend?

EIA 2012 and 2009 World Energy Outlook, U.S. Census
Chemical data from DOE/EIA 2006 Manufacturing Energy Consumption Survey (MECS) and T.K. Swift, American Chemistry Council "Updated Energy Slides Incorporating 2008 Data"

Solar Energy Quiz

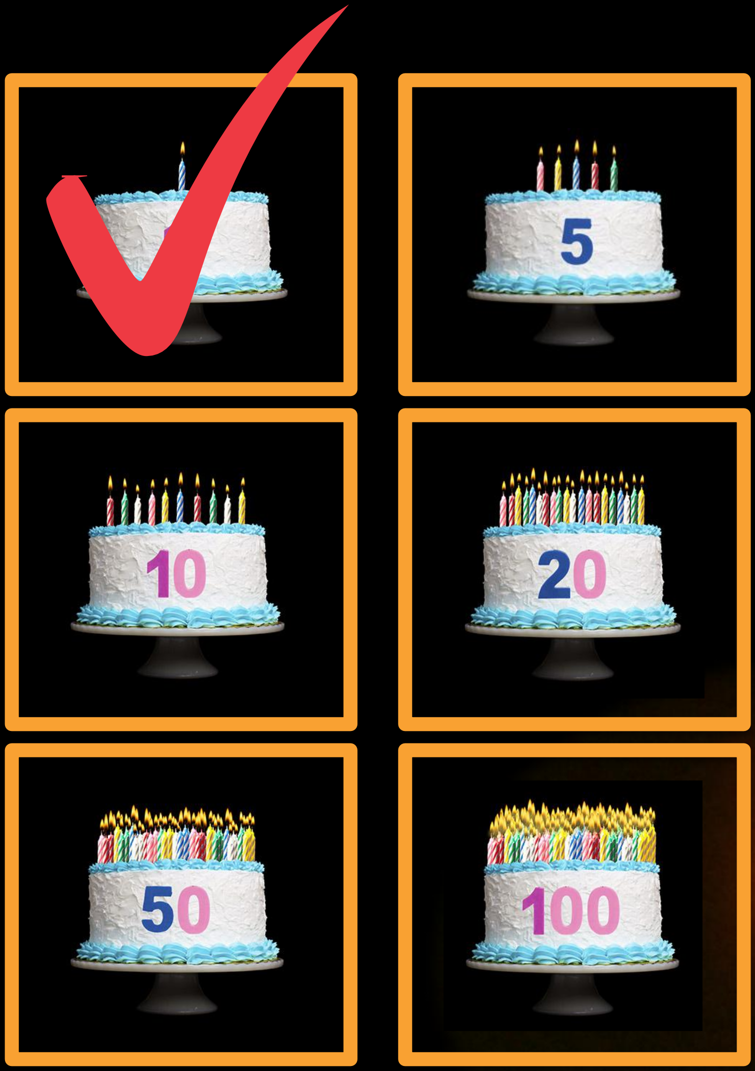
? =



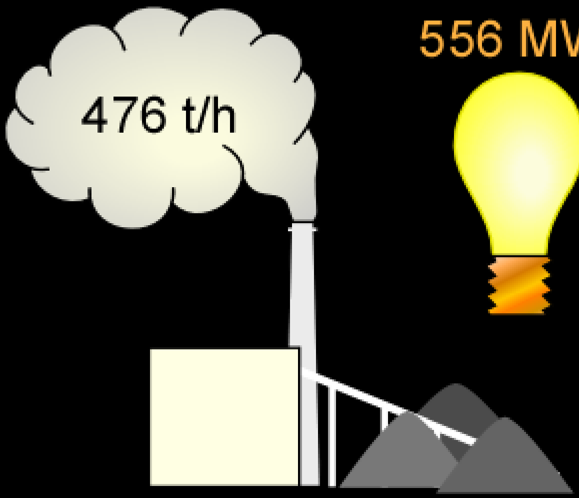
Solar Energy Quiz

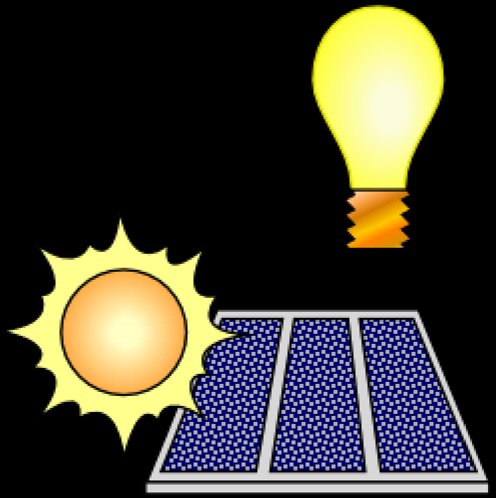
?

=



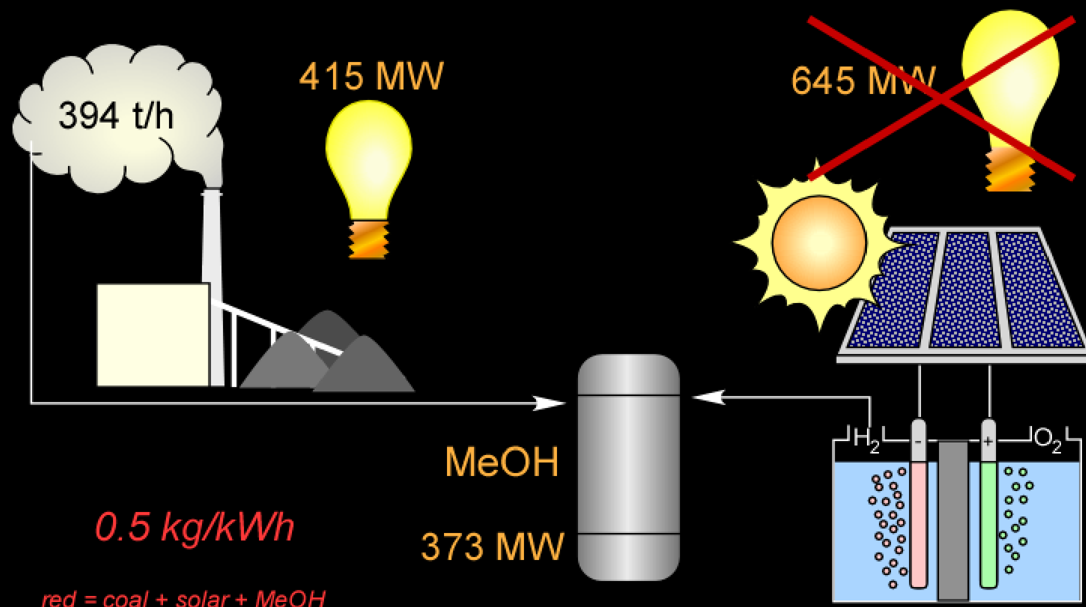
CO_2 Utilization



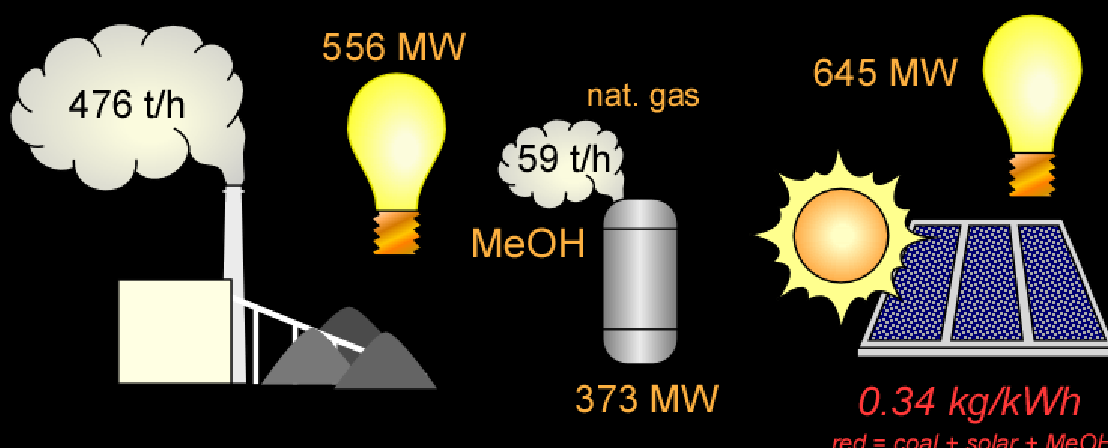


Just Not Practical

0.4 kg/kWh



DOI:10.3303/CET1229078 Van-Del and Bouallou



Possible, Not Economical

image from carbonengineering.com, 14 Jan 2013.

Skyonic

CALERA
Green Cement for a Blue Planet

Carbon Engineering seeks to scrub atmospheric CO_2 by using alkaline solutions that are dried and thermally regenerated.

$$2\,NaOH_{(aq)} + CO_{2(aq)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)}$$

$$Na_2CO_{3(aq)} \xrightarrow{\text{heat}} 2\,NaO + CO_2$$

$$2\,NaO + H_2O_{(l)} \longrightarrow 2\,NaOH_{(aq)}$$

Possible, Not Economical

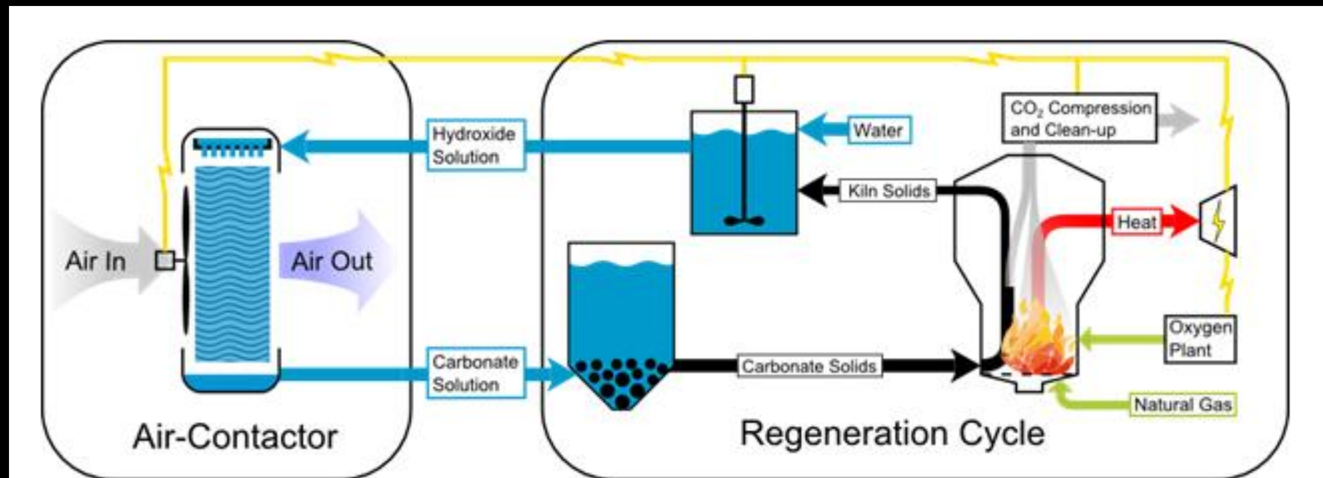


image from carbonengineering.com, 14 Jan 2013.

$$2\ NaOH_{(aq)} + CO_{2(aq)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)}$$

$$Na_2CO_{3(aq)} \xrightarrow{\text{heat}} 2\ NaO + CO_2$$

$$2\ NaO + H_2O_{(l)} \longrightarrow 2\ NaOH_{(aq)}$$

Problem: fuel use makes >50% of the CO_2 the system can scrub
Problem: CO_2 has no value (this is an added COST)

A Look at Biofuels

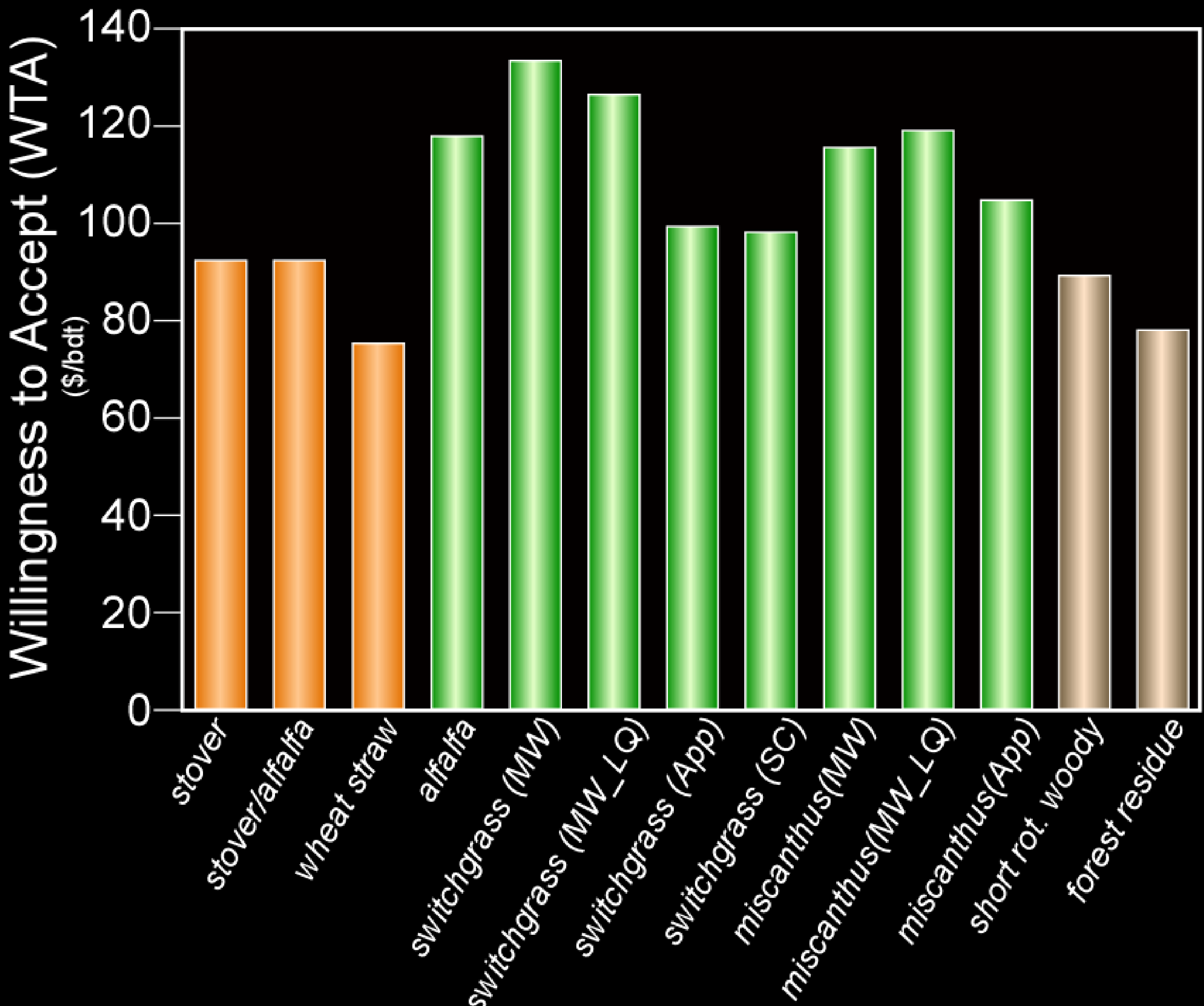
BIOMASS FUELS PROGRAM

Consider the Biofuels Challenges

- **How much biomass is available?**
  Not enough to replace fossil fuels
- **How much will biomass costs?**
  It is not cheap
- **How much will biofuels cost?**
  More than fossil
- **How much more are we willing to pay?**
  No premium

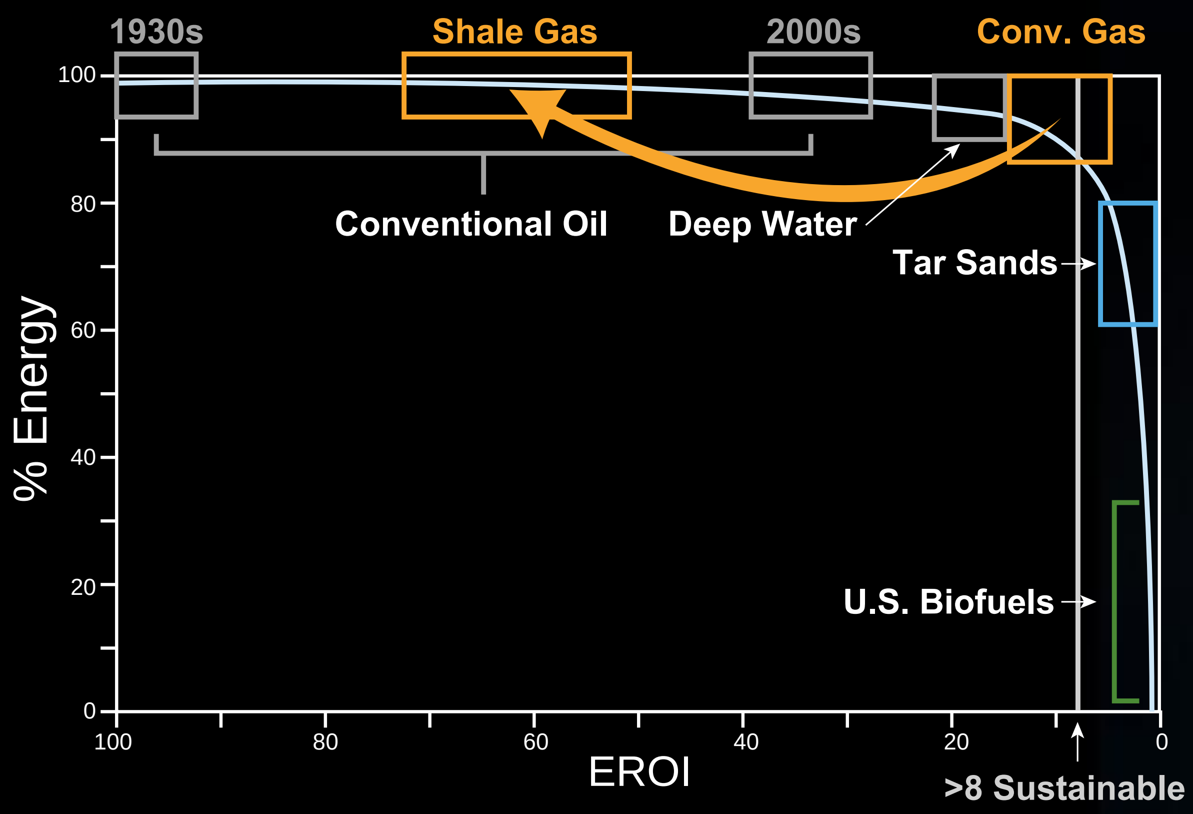
CELLULOSIC
ETHANOL

Cost of Biomass Feedstock



NRC, "Renewable Fuel Standard: Potential Economic and Environmental Effects of U.S. Biofuel Policy", 4 October 2011.

Thermodynamic Entitlement

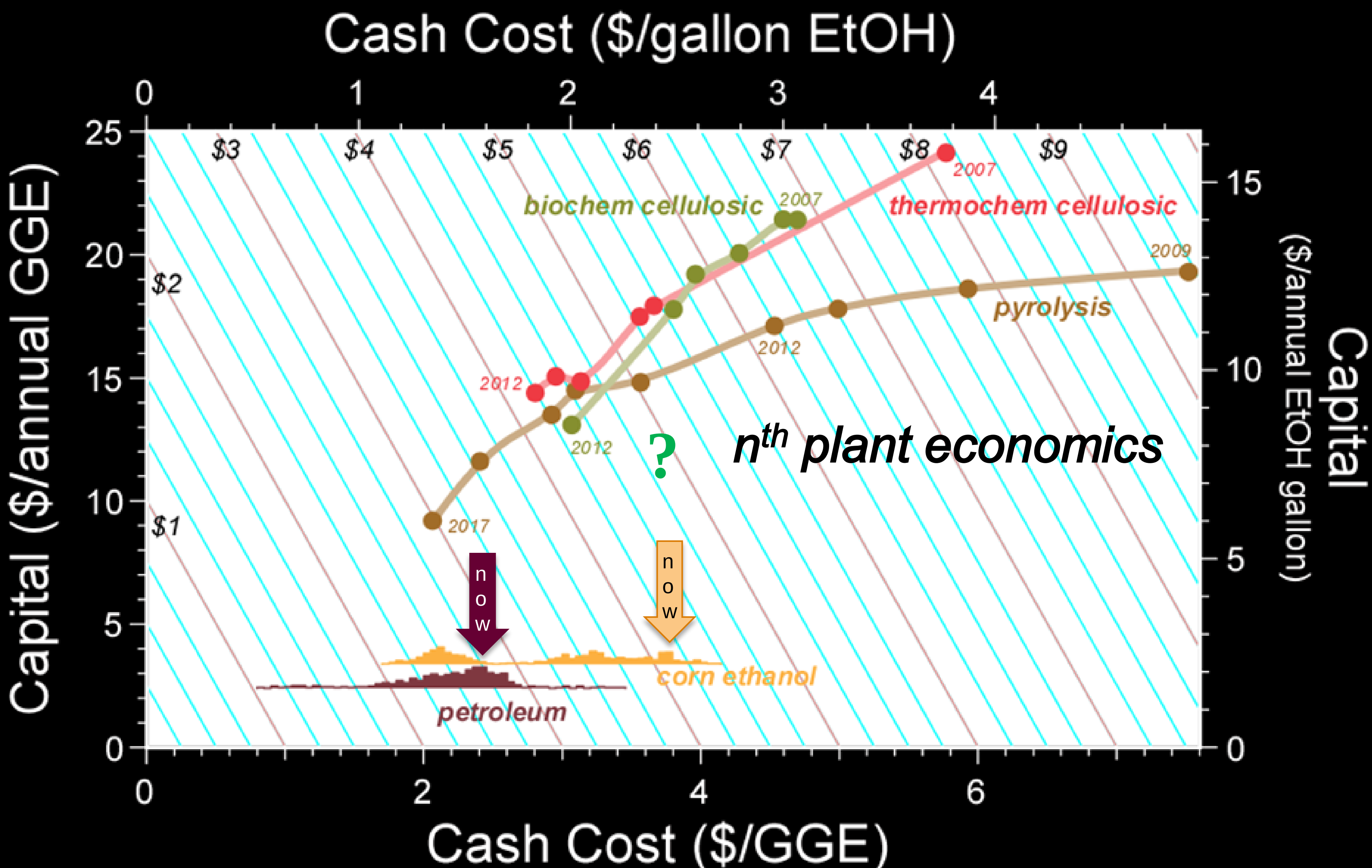


Energy return is a key parameter when the products are fuels.

Shale goes against recent trends.

Suggested reading: Guilford, M.C.; Hall; O'Conner, P.; Cleveland, C.J. A New Long Term Assessment of Energy Return on Investment (EROI) for U.S. Oil and Gas Discovery and Production. Sustainability 2011, 3(10), 1866-1867.

DOE Estimates



DOE OBP April 2011 and Nov 2012 MYPP with constant feedstock of $100
Escalated to 2013 dollars.

Biofuels

DOW

arpa·e
CHANGING WHAT'S POSSIBLE

Plants Engineered to Replace Oil

- <u>Thermodynamic realities</u>
- solar flux is limiting
- photosynthetic efficiency is limiting
- land is limited and best places already grow food
- conversion of plants to fuel is inefficient

Pivot to Biomaterials

BIOMASS FUELS PROGRAM

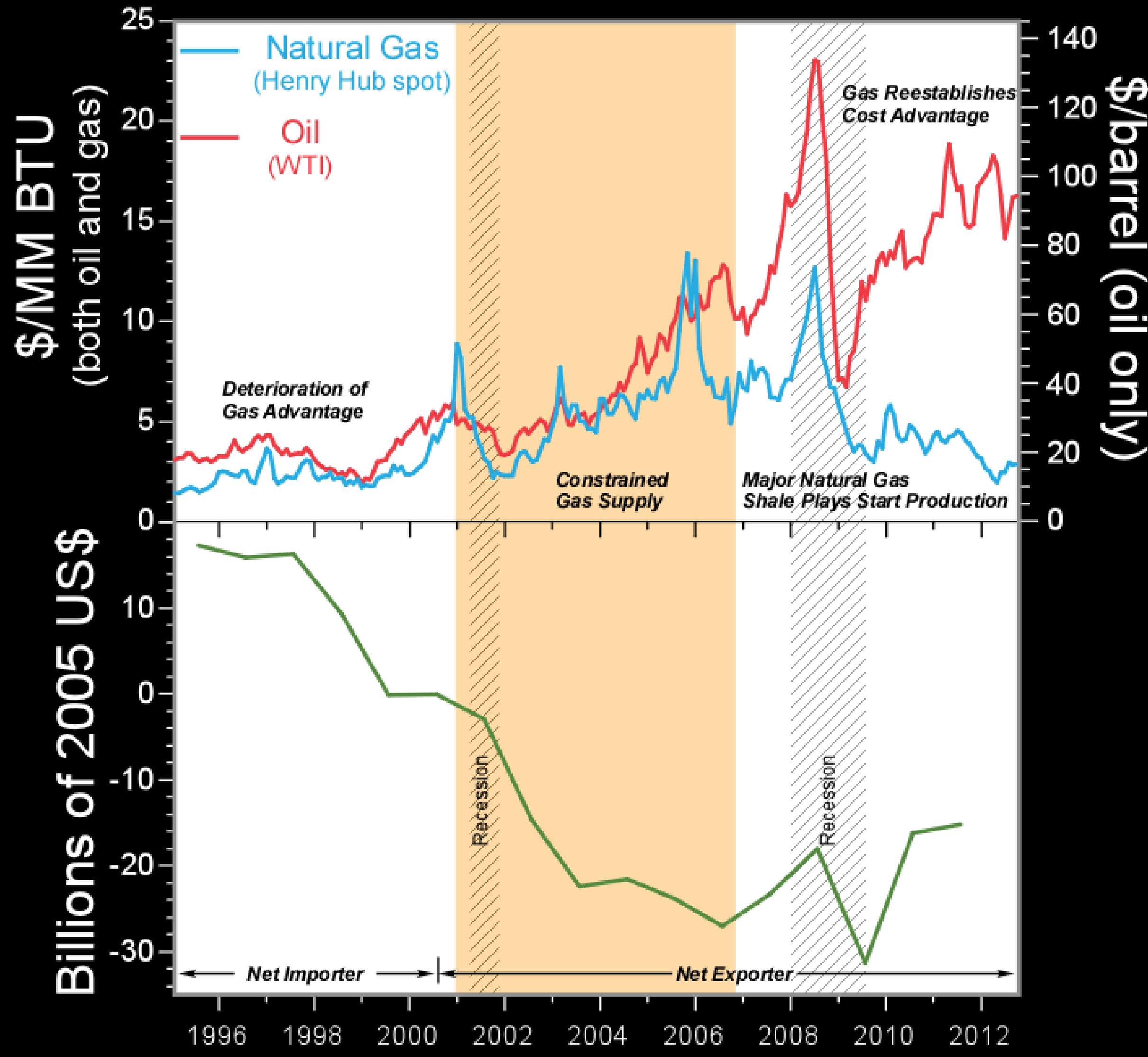
SCALE ISSUES

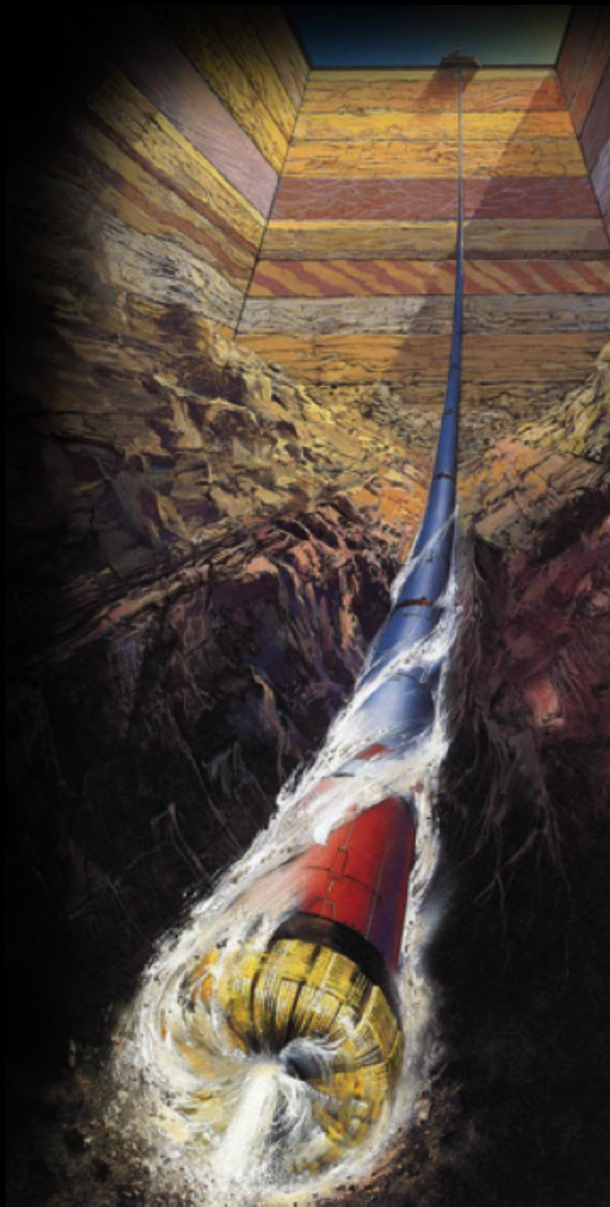
AMYRIS

SCALE ISSUES

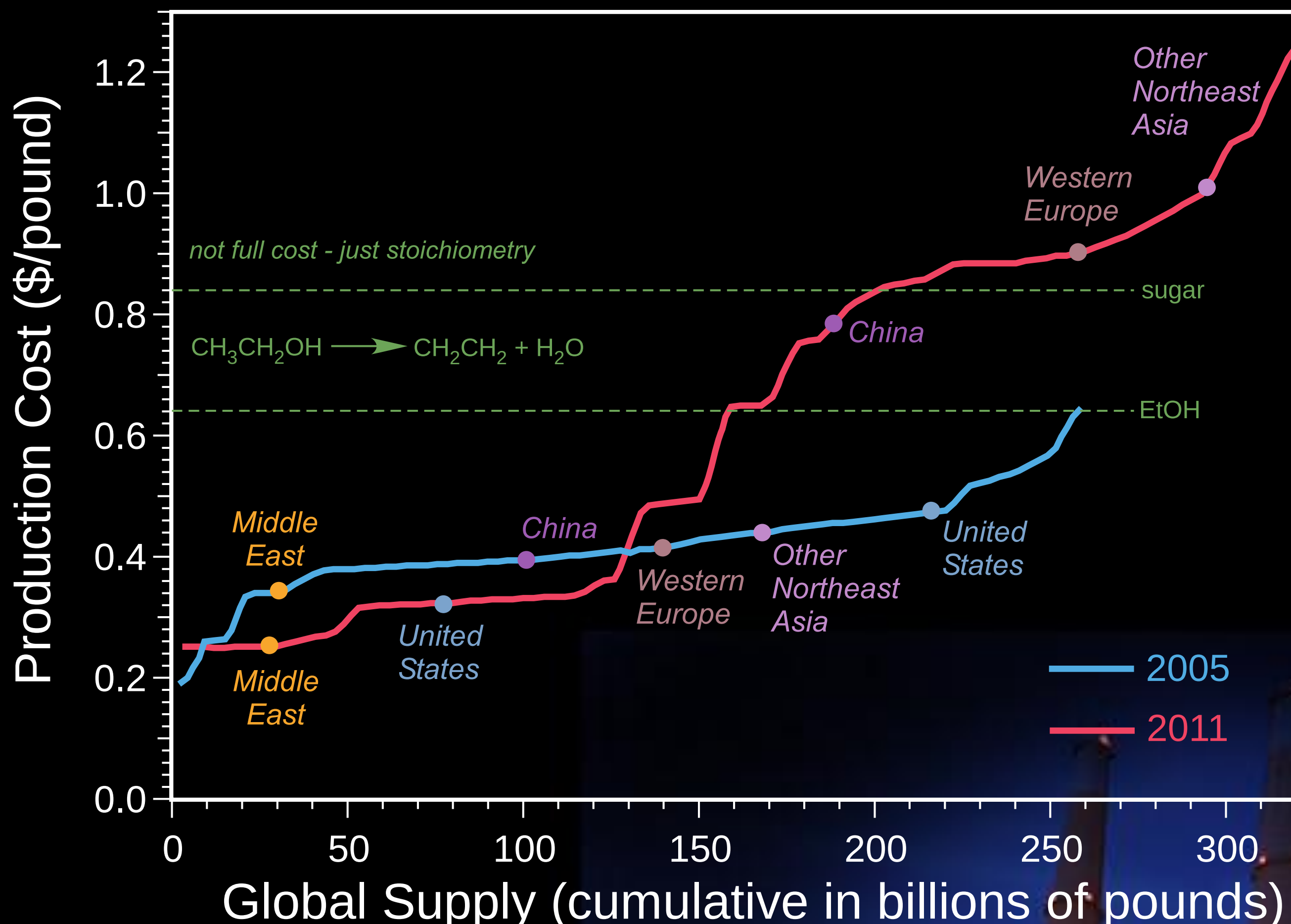
BIOMATERIALS PROGRAM

Chemical Industry is Rejuvenated



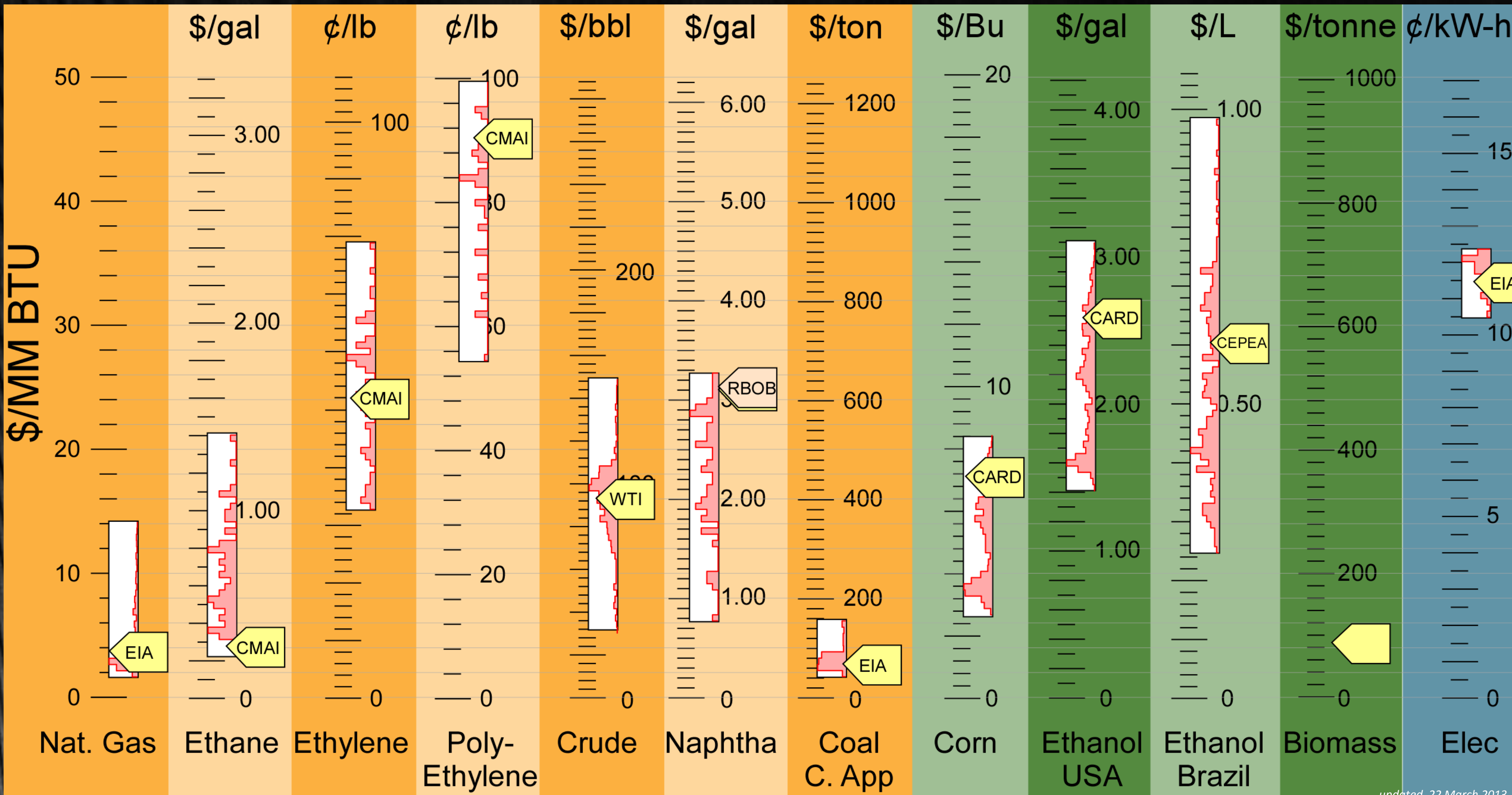


Impact of Low Gas Prices

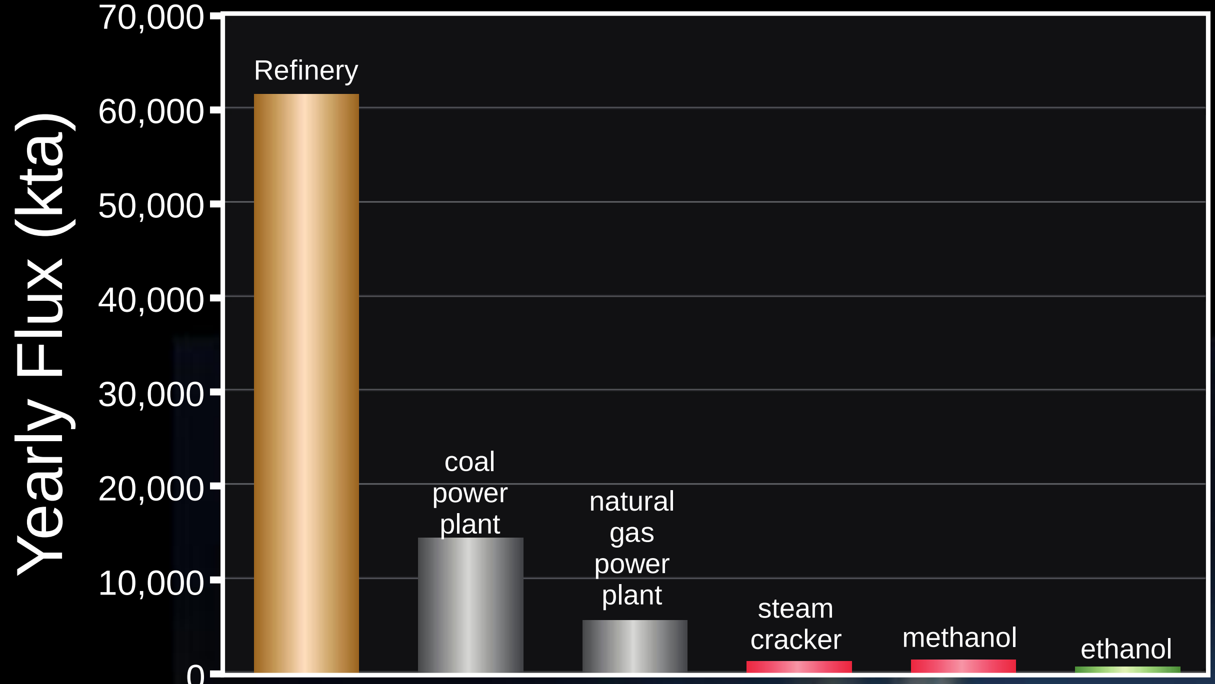


Owen Kean and T.K. Swift, American Chemistry Council, "Industry-Transforming Natural Gas into Products", National Academy Forum on Unconventional Gas, 11 September 2012.
Ethanol and Sugar from 10 Jan 2013 prices sugar is average of monthly close for 2011; EtOH is average of daily close for 2011.

An Honest Look at Energy Content



Energy Happens at Large Scale



The Importance of Scale

Scale reduces the cost of production when materials are consumed or produced.

Green Design and LCA Rankings Don't Match Up

Biopolymers rank in the middle of LCA rankings

Polymer	Material	Green Design Rank	LCA Rank
Polypropylene	Fossil fuels	9	1
HD Polyethylene	Petroleum	5	2
LD Polyethylene	Petroleum	7	3
Polyhydroxyalkanoate-Stover	Cornstalks	2	4
General Purpose Polystyrene	Petroleum	10	5
Polylactic Acid – NatureWorks	Sugar/cornstarch	1	6
PVC	Chlorine/petroleum	11	7
Polyhydroxyalkanoate-General	Corn kernels	2	8
Polylactic Acid-General	Sugar/cornstarch	4	9
PET	Petroleum	6	10
Polycarbonate	Petroleum	12	11
Bio-PET	Petroleum/plants	8	12

Tabone, MD; Cregg, JJ; Beckman, EJ; Landis, AE. Environ. Sci. Technol. 2010, *44*, 8264-9.

BIOMATERIALS ≠ BIOFUELS

BIOMATERIALS PROGRAM

Materials Science Success:
DOW POWERHOUSE™ Solar Shingles

POWERHOUSE™
Dow SOLAR

FILMTEC™ Modules for Water

Energy savings on water purification

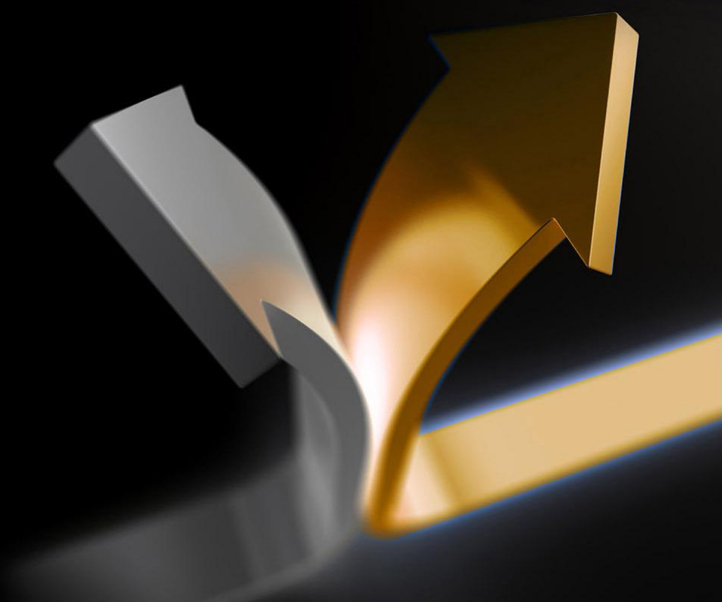
Process	Operating Energy Consumption (Kwh/m^3)	Customer Energy Savings 2005-2015 (Barrels of Oil-eq)
Multi Stage Flash (MSF)	13.5 - 25.5	242 million
Multi Effect Distillation (MED)	6.5 – 11	82 million
Reverse Osmosis	3 - 3.5	

Biofuels and Clean Tech Conclusions

- Too much hype for the possible, not enough focus on the practical
  - Incumbent fossil sources set the standard for competition
  - It takes decades to deploy a new technology
  - Biomass availability limits biofuels scale
- Move to bioproducts needs scrutiny
- Fundamental engineering judgment is crucial to long-term innovation
- Materials solutions will enable viable energy options

> “Facts are the air of scientists.
> Without them you can never fly.”
>
> Linus Pauling

Thank You

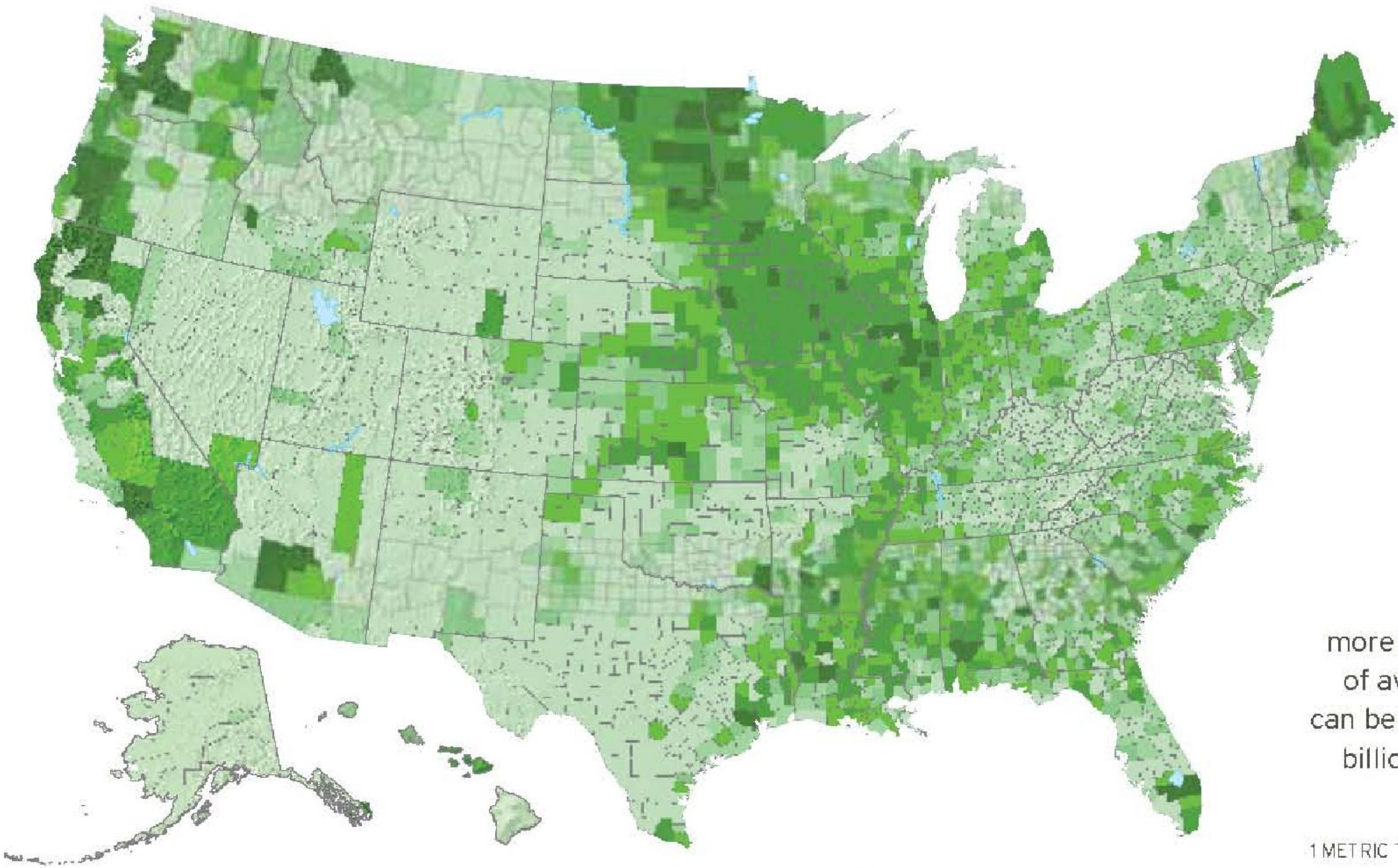


Biomass Resource

DOW

Cellulosic Ethanol

The '50-State' Solution

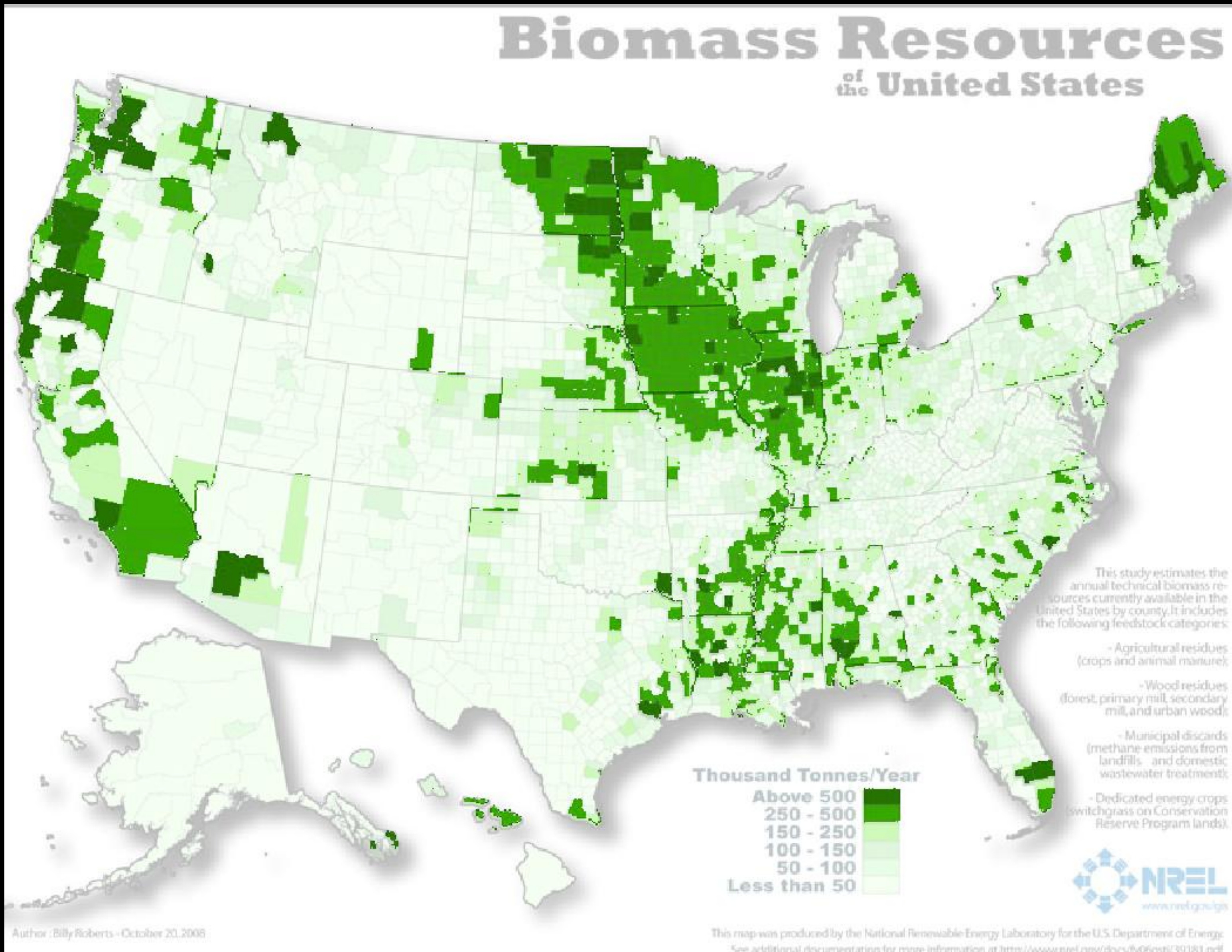


It's everywhere

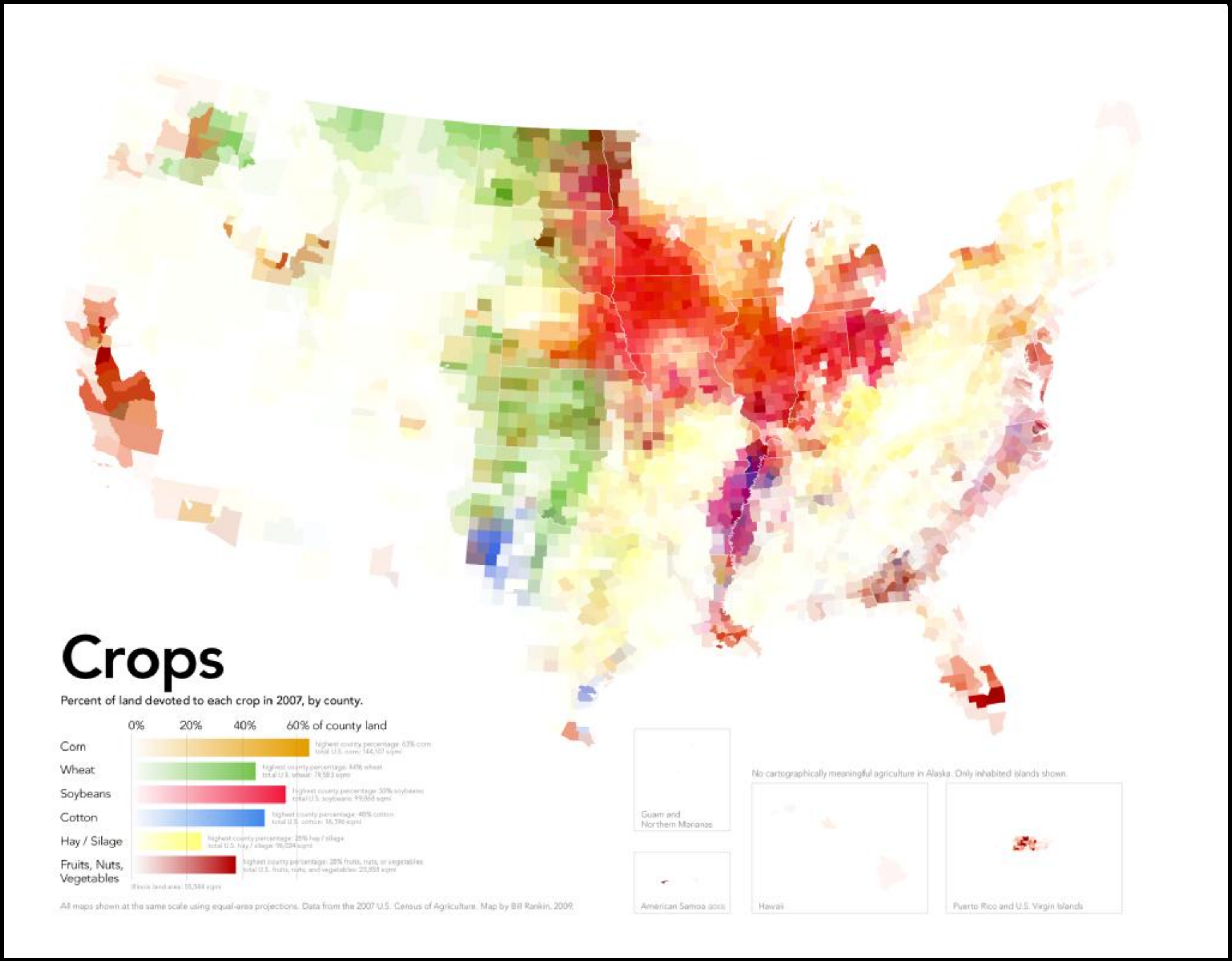
The U.S. is home to more than one billion tons of available biomass that can be converted to 80-100 billion gallons of ethanol.

1 METRIC TON = 1.1 TONS; SOURCE: NREL

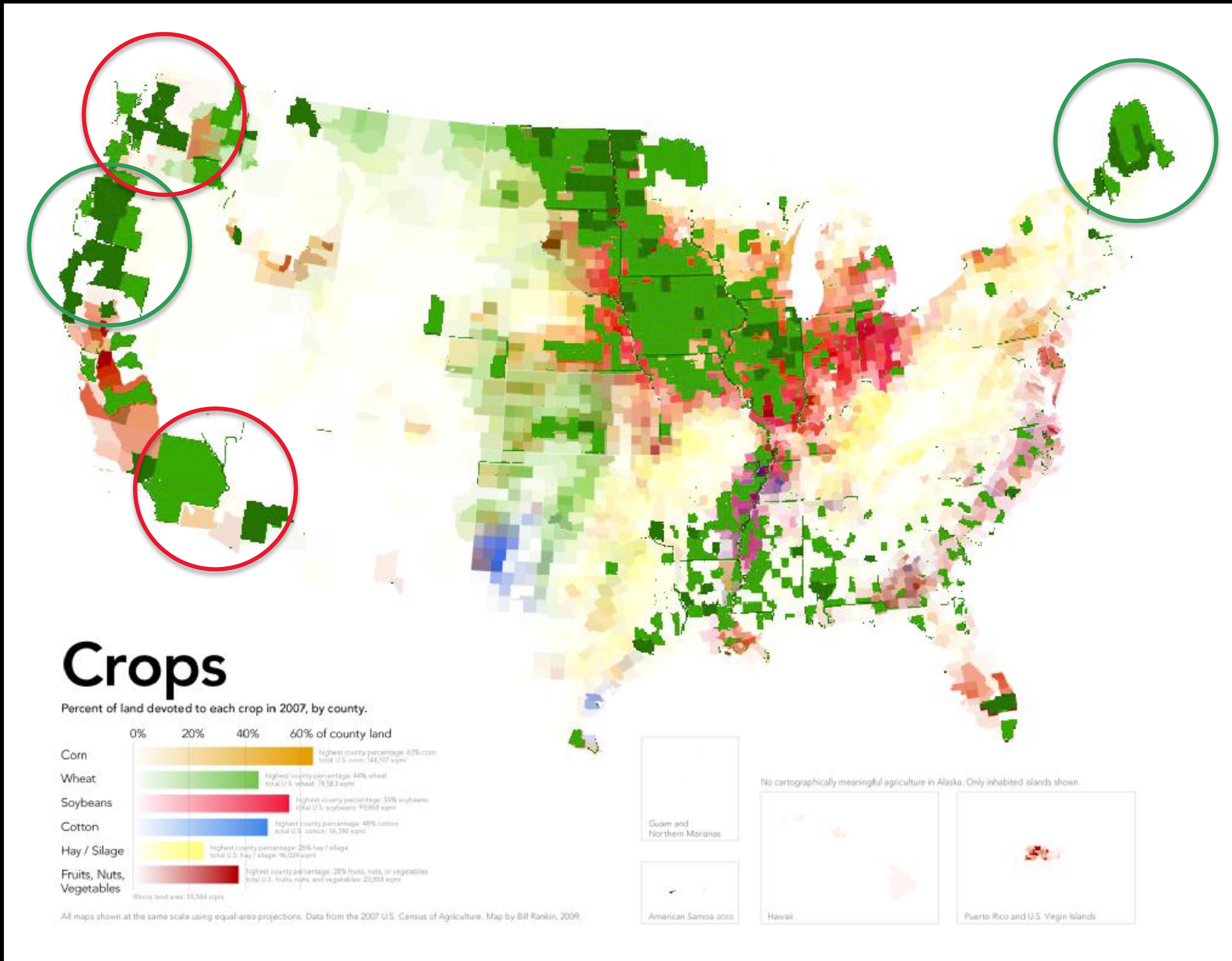
Is It Really Everywhere?



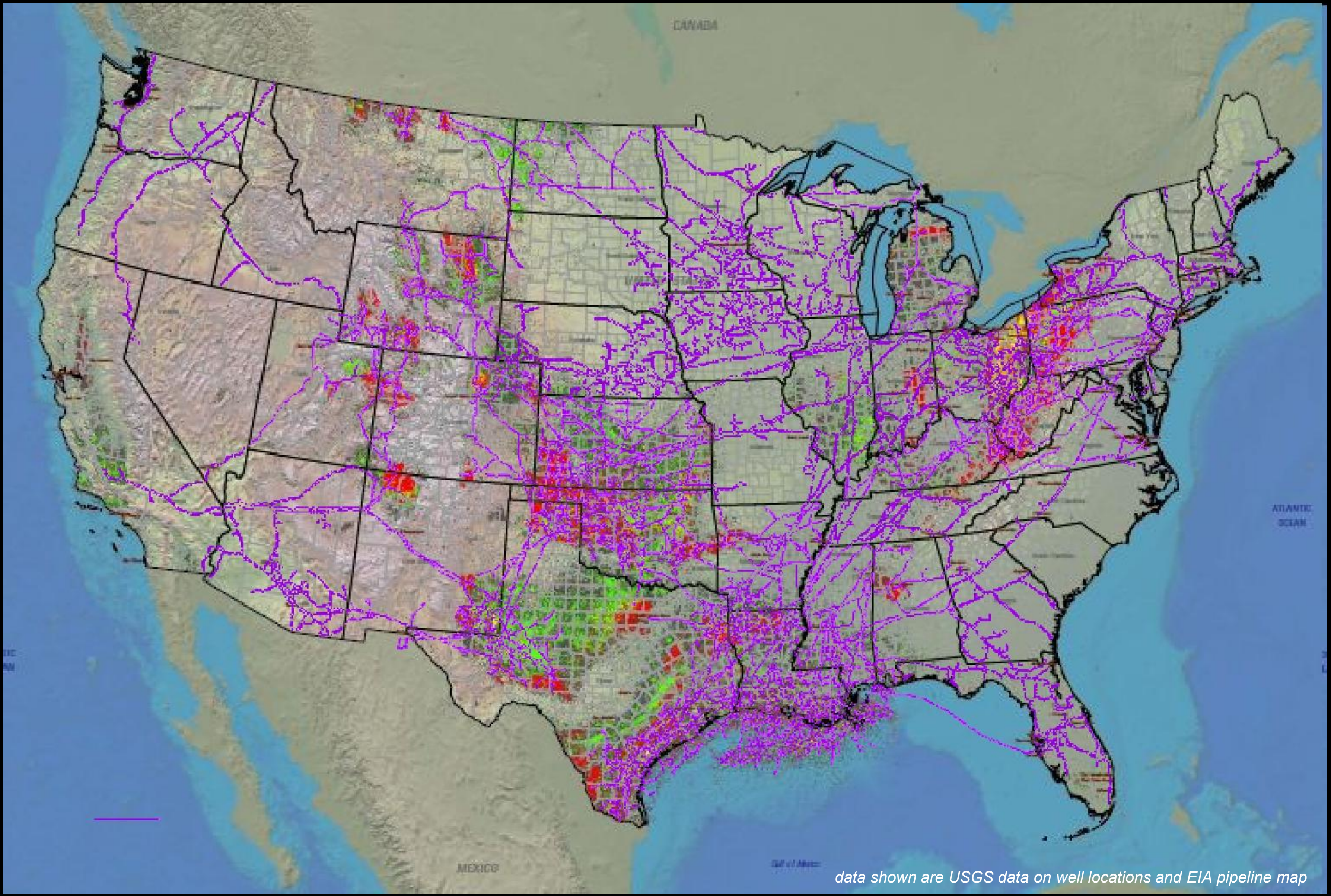
Currently Used Land



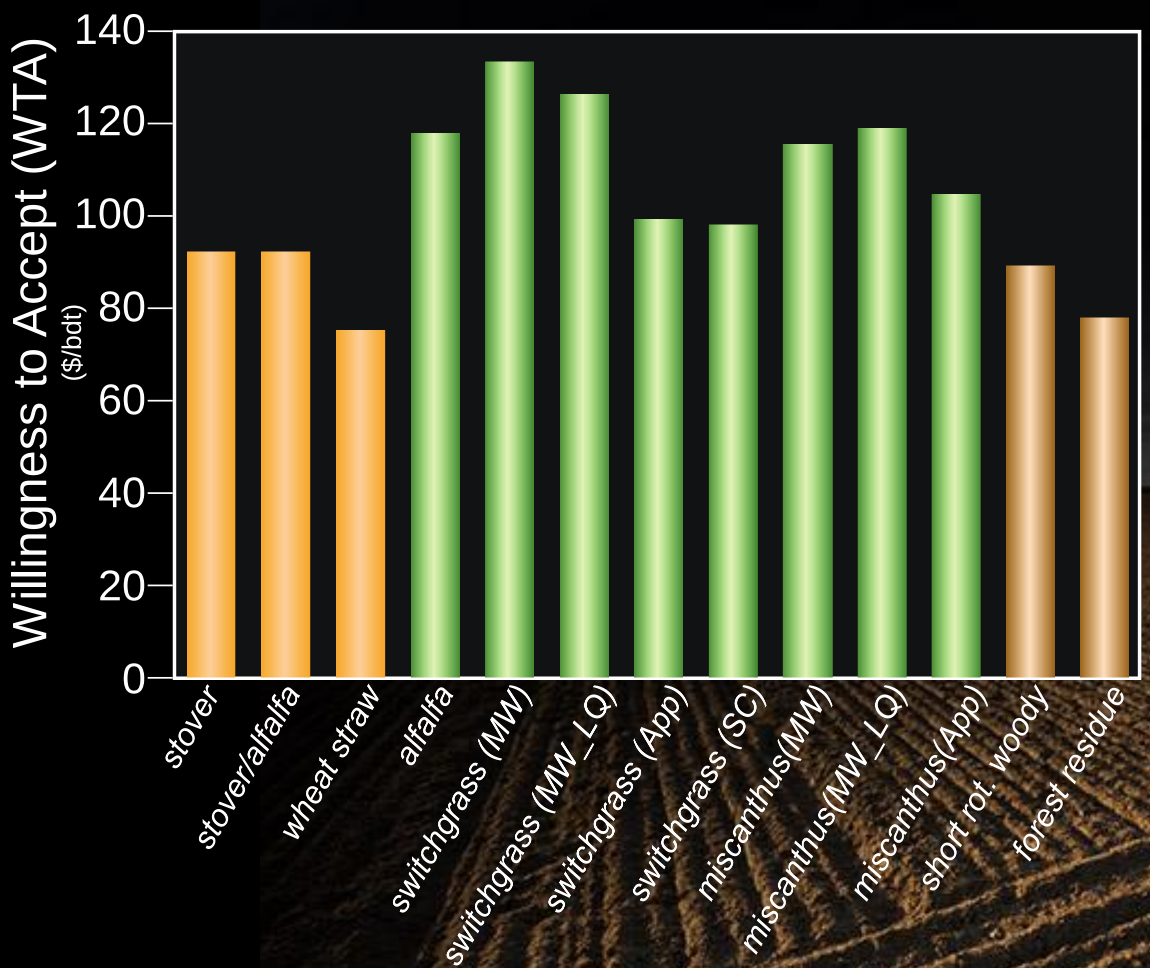
Currently Used Land



Oil and Gas Infrastructure



Biomass Cost: Farmers Are Practical, Too



Landowners/farmers have finite land and time. They will not plant lower value crops and sacrifice return off the land.

NRC, “Renewable Fuel Standard: Potential Economic and Environmental Effects of U.S. Biofuel Policy”, 4 October 2011.

Bio Fads

“The art of being wise is the art of knowing what to overlook.” – *William James*

Hydrogen Car

"We asked ourselves, **'Is it likely in the next 10, 15, or 20 years that we will convert to a hydrogen car economy?'** The answer, we felt, was 'no.'”

Steve Chu, Energy Secretary, May 2009

Corn Ethanol

“…Using land to grow fuel leads to the destruction of forests, wetlands and grasslands that store enormous amounts of carbon.”

Michael Grunwald, TIME, April 2007

Biodiesel

“Biofuels are contributing to higher prices and tighter markets.”

Timothy Searchinger, Princeton University, April 2011

Cellulosic Ethanol

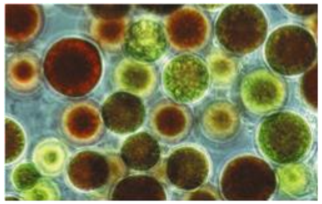
“…the need for trucks, machinery and manpower would come during harvest, already the busiest time of the year on the farm. And that’s where a massive federal initiative into cellulosic ethanol may find its biggest bottleneck – on the farm.”

Robert Rapier

Algae

“…microalgae can be raised on cheap, sun-splashed land that is unsuitable for crops or much of anything else.”

Paul Voosen, New York Times, 29 March 2011.



Bio Plastics

Dow launched the JV with Cargill in 1997 to develop and market PLA from corn; we exited the JV in 2004.

NatureWorks

Dow Cargill

THE WALL STREET JOURNAL.

“Sun Chips Bag to Lose Its Crunch”

Bio-based packaging launched in 2009 was discontinued by late 2010, due to performance perception issues.

Photo: Associated Press

Glycerin to Epi

Dow postponed in 2009 due to uncertain supply.

Dow

Natural Oil Polyols

RENUVA™

Dow launched in 2007, exited in 2010.

Dow

ADM-Metabolix

ADM has given notice of termination of the Telles, LLC joint venture for PHA bioplastics.

Metabolix

What Impact?

plantbottle

100% renewable PET (not yet available) would required ~80 2 L bottles to offset burning 1 gallon of gasoline or about 400 at today's 30%

material	per capita consumption (lb/yr)
PET packaging	17
petroleum	6619
natural gas	8037
coal	6439
gasoline	2495
sand and gravel	13923
cement	512
iron ore	340
salt	403
beef	54.3
chicken	55.7

Which Uses Less Total Energy to Go a Mile?

2011 Compressed Natural Gas Civic

U.S. Average Gas

2011 Leaf Electric Vehicle

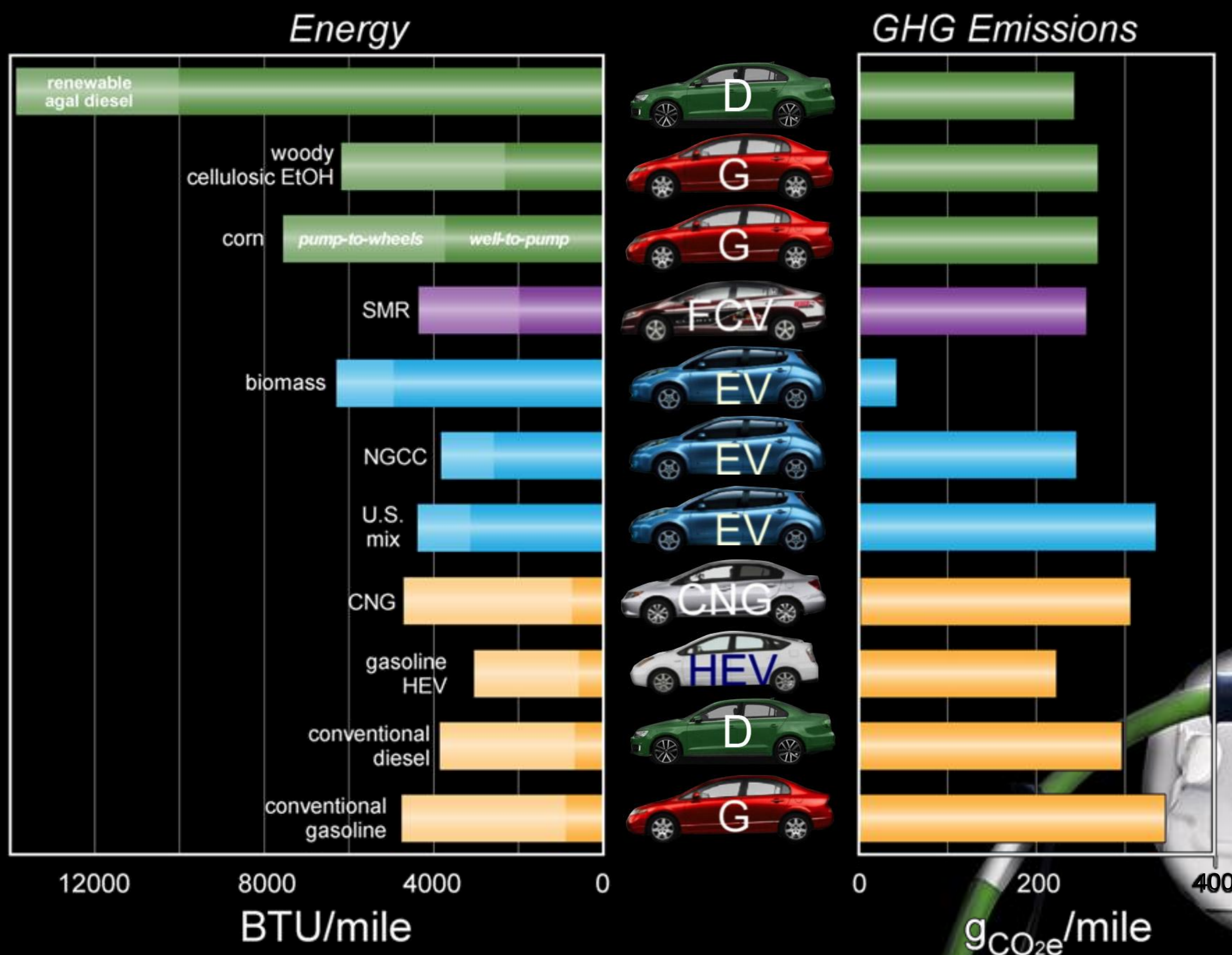
U.S. Average Power

Natural Gas Combined Cycle

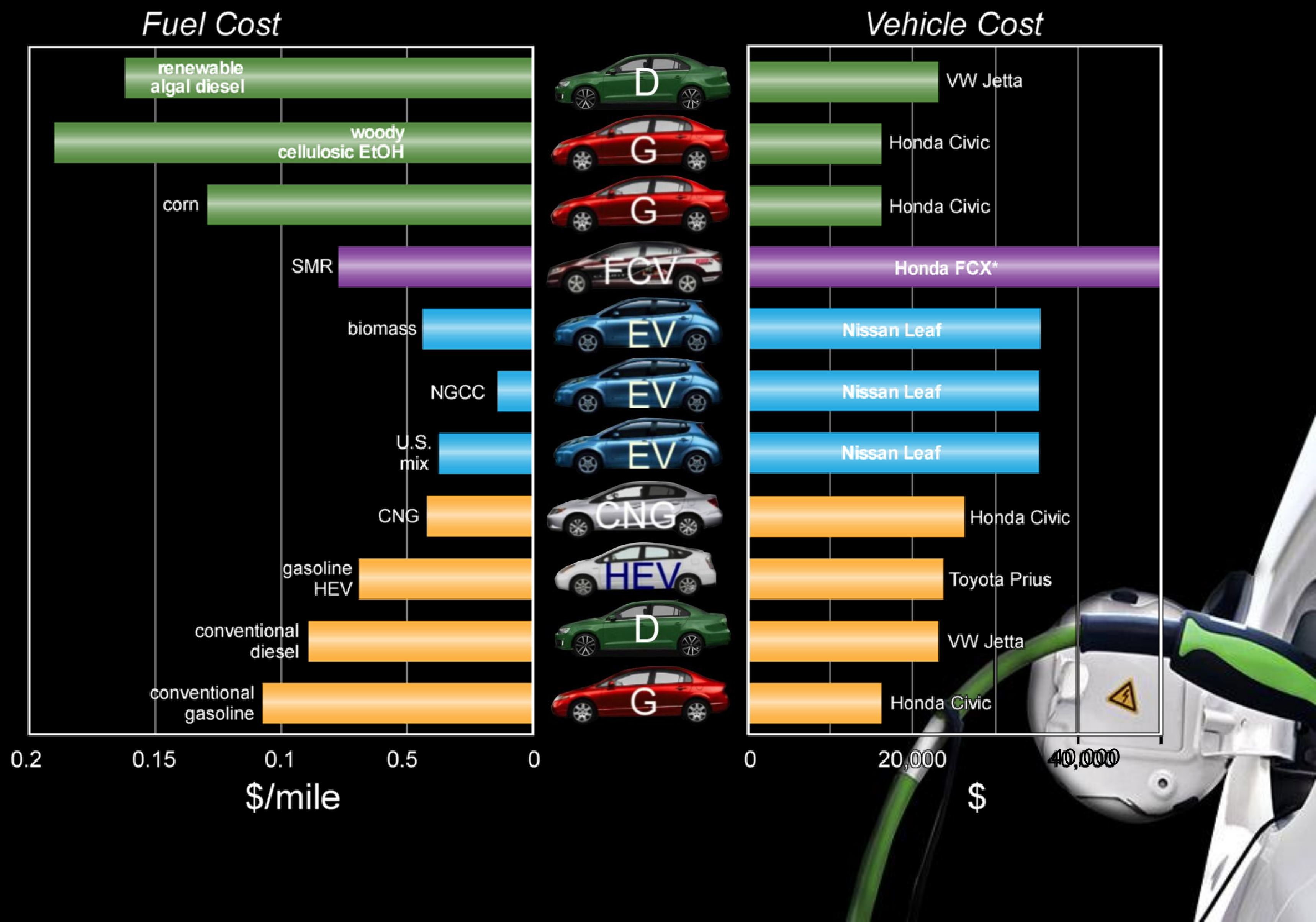
2011 Civic Using E-85

Current Corn Ethanol

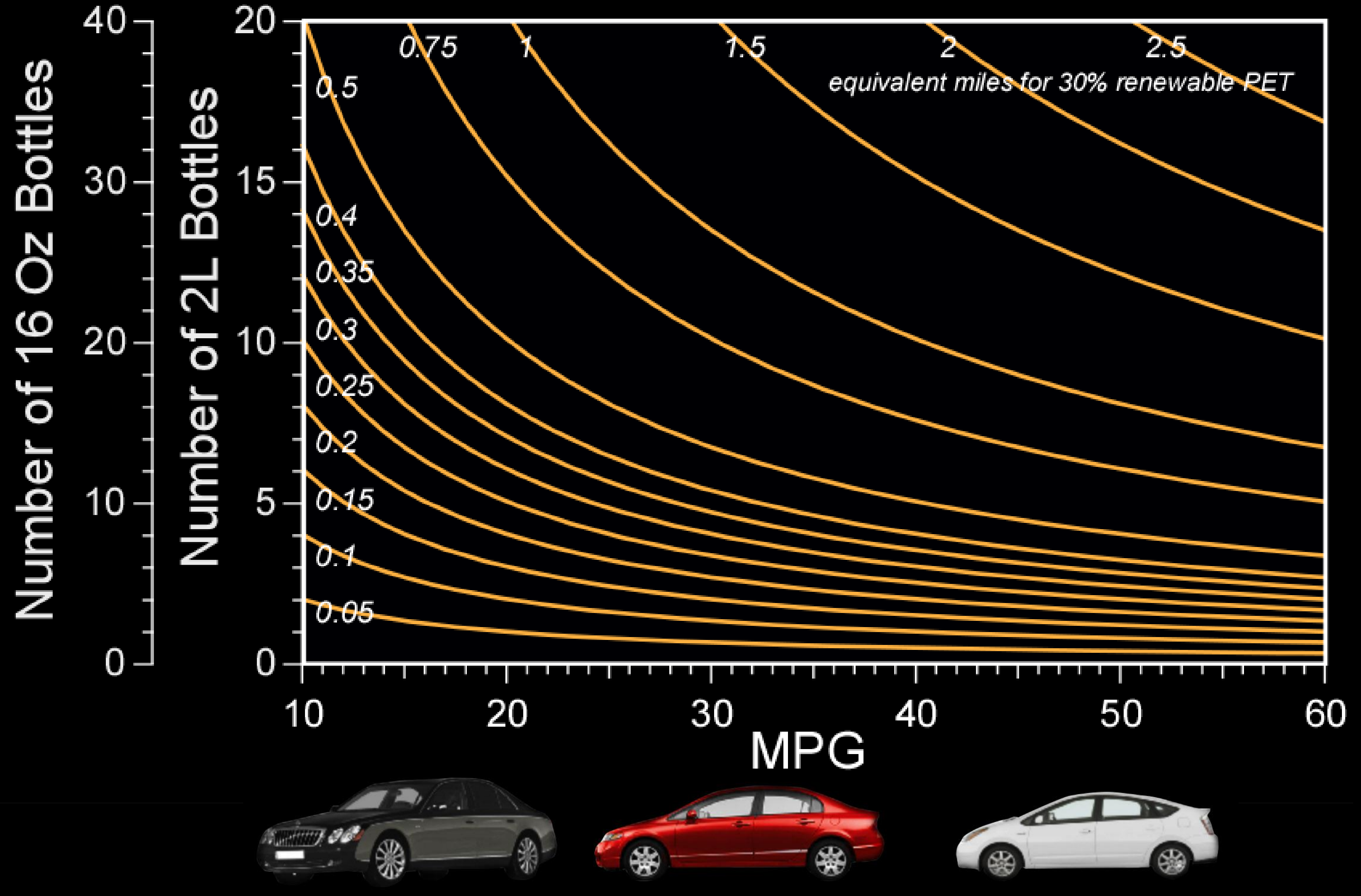
Electrification Beats Biofuels (Impact)



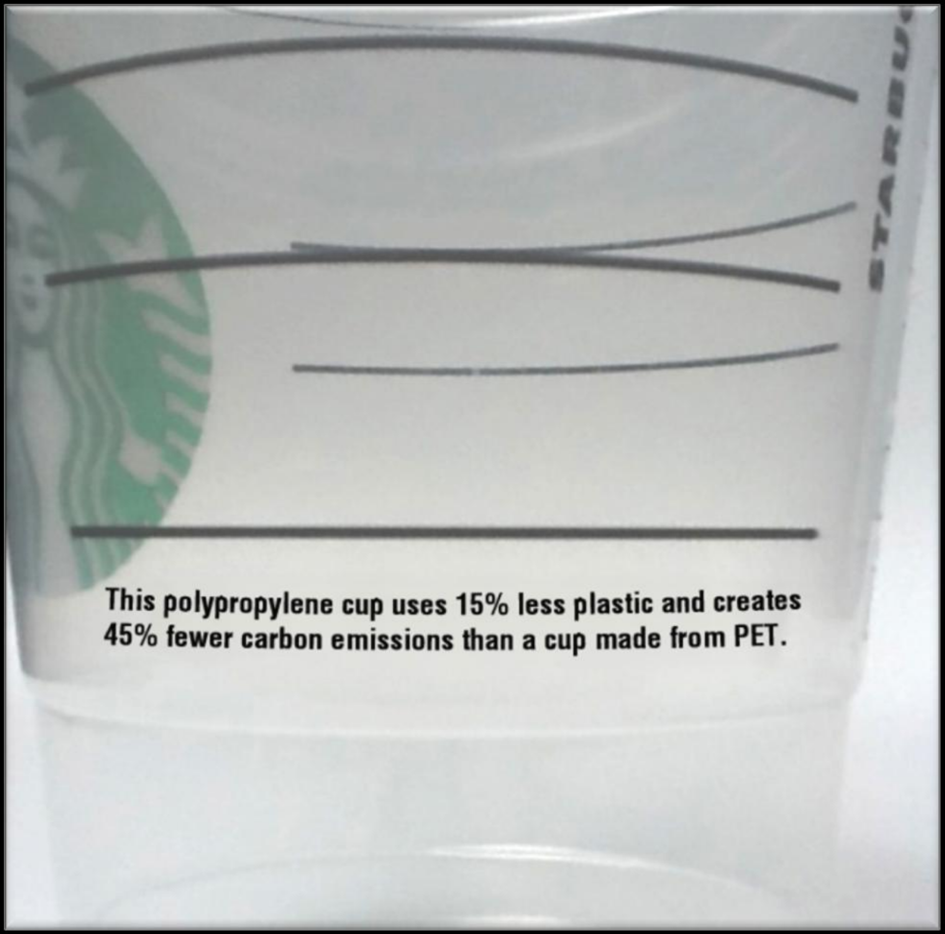
Electrification Beats Biofuels (Costs)



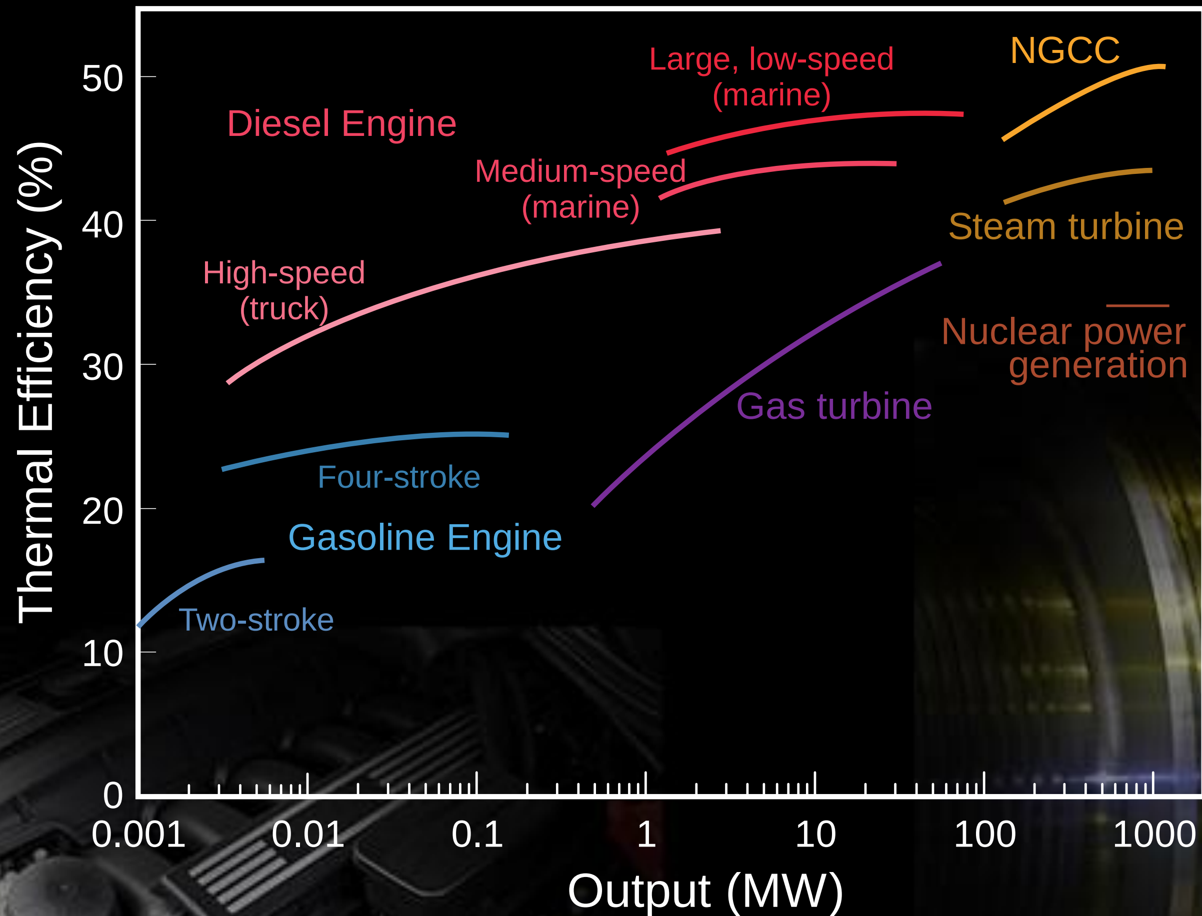
PET Comparison



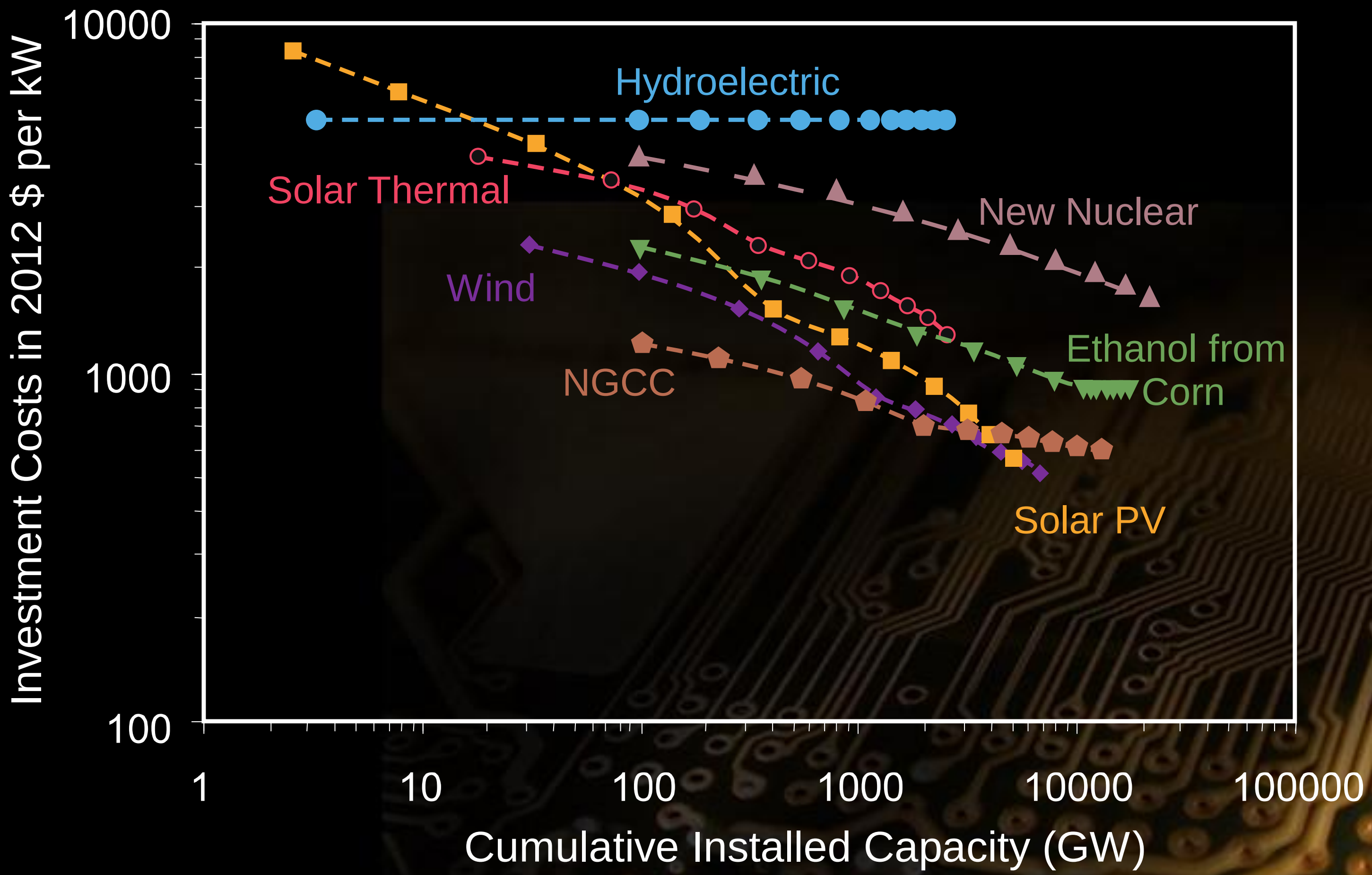
Signs of Hope



Scale Improves Efficiency

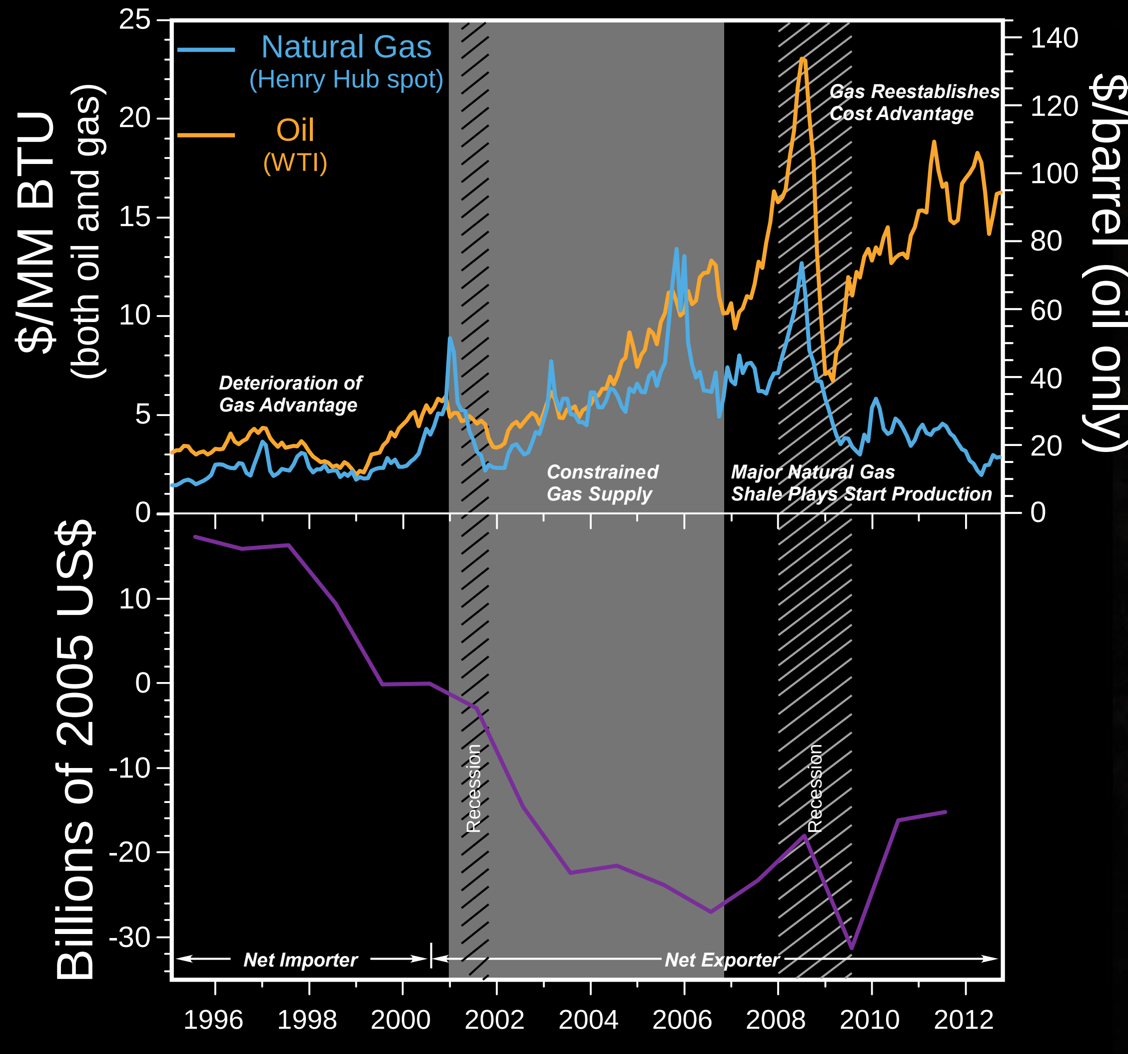


Experience Curves



Adapted from Riahi et al., Energy Economics 26 (2004) 539-564.

Chemical Industry is Rejuvenated



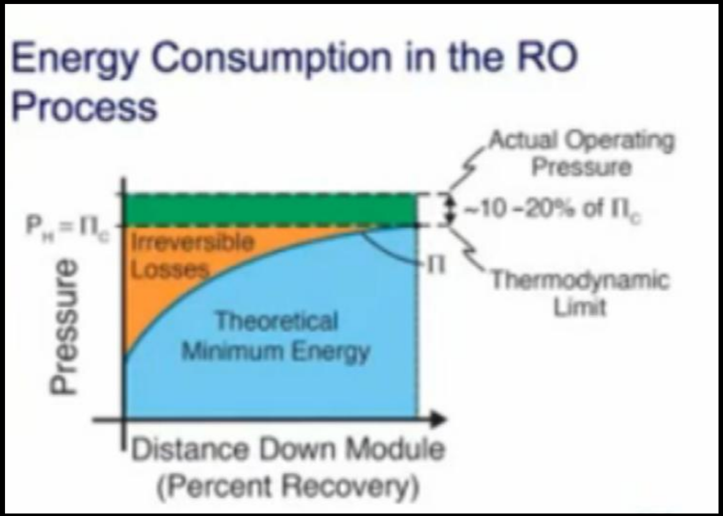
Desalination

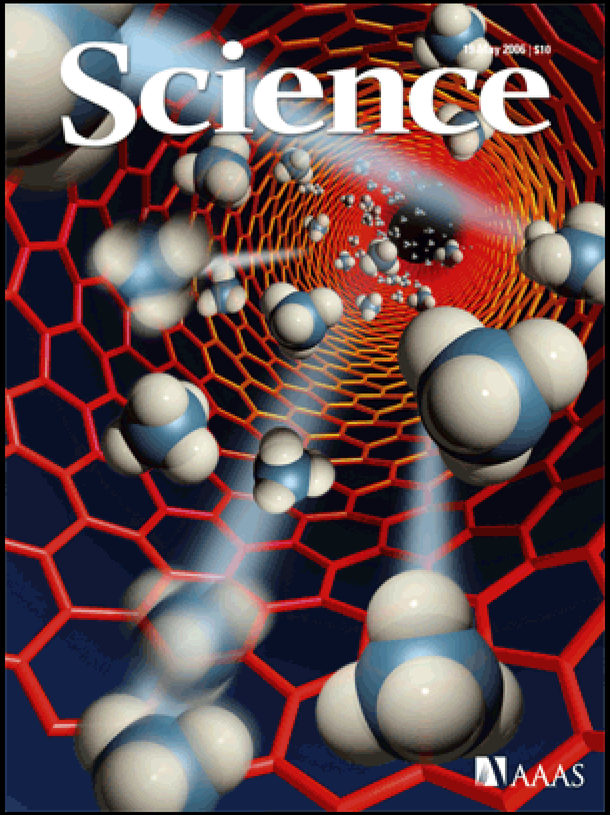
"NanOasis proposes to utilize carbon nanotubes (CNTs) to make industrially-scalable reverse osmosis (RO) membranes ….We target a ten-fold permeability increase compared to today's commercial state-of-the-art, resulting in a 30-50% energy savings…"

$$-d\left(\Delta G_{mix}\right) = -RT \ln a_w dn_w = \pi v_w dn_w$$

$$E_{thermo,\min} = \frac{V_0 \int_0^R \pi dR}{V_0 R} \quad \text{or} \quad \frac{1}{R}\int_0^R \pi dR$$

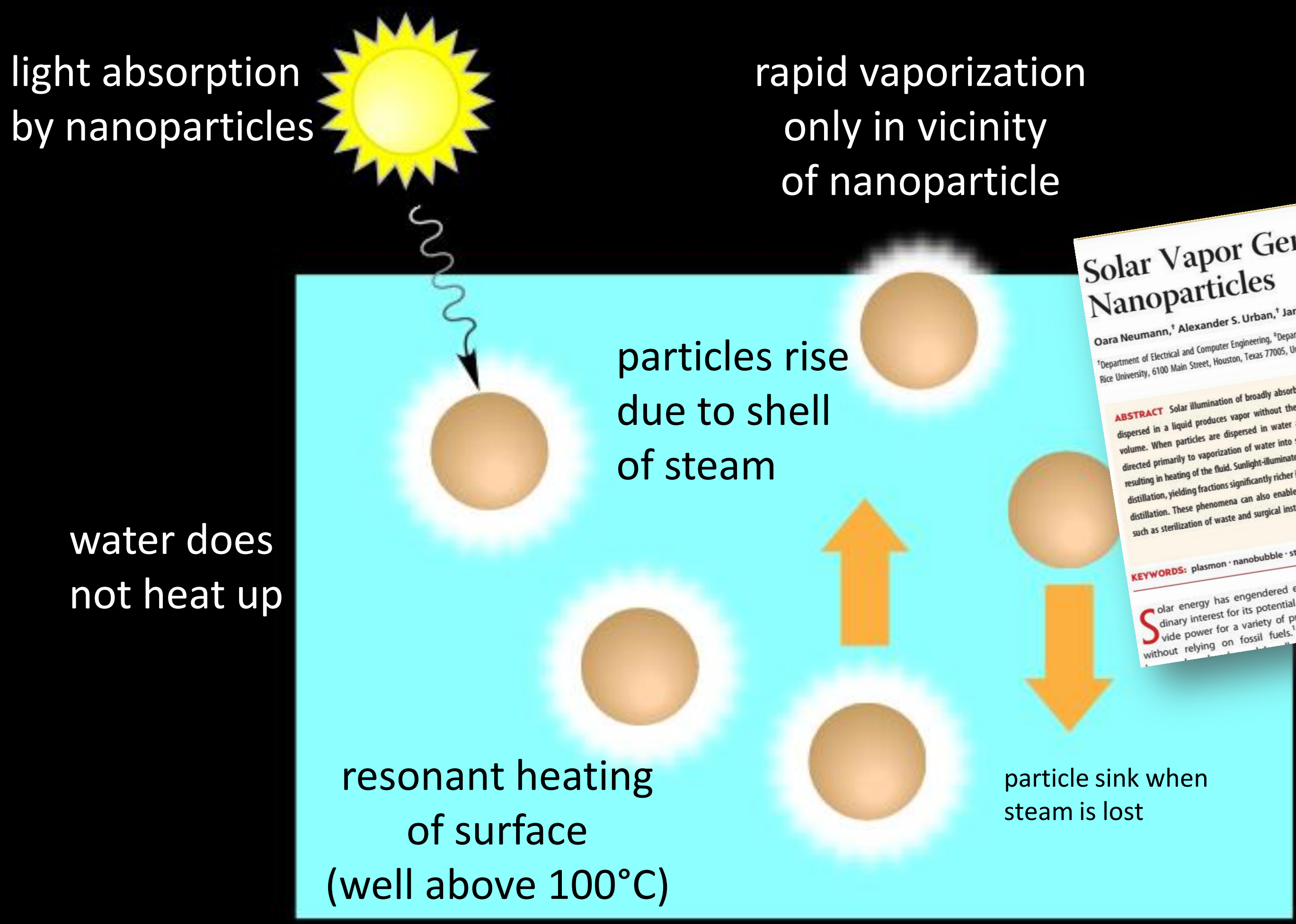
a_w=activity of water
n_w=moles of water
v_w=molar volume of water
π= osmotic pressure

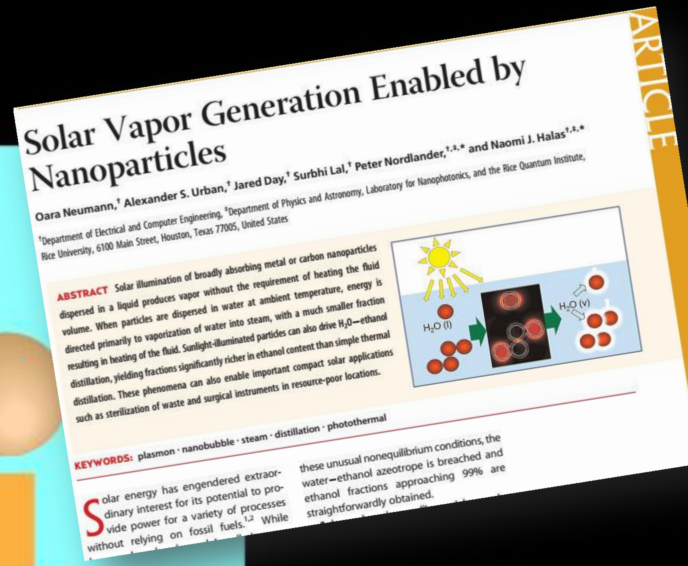




<u>50% Recovery of Seawater (3.5% salt)</u>
Current RO Energy Efficiency ~1.8 kWhr/m^3
Theoretical Energy Efficiency = 1.1 kWh/m^3
(literature values from 0.98-1.06)

Possible





ARTICLE

Solar Vapor Generation Enabled by Nanoparticles

Oara Neumann,[†] Alexander S. Urban,[†] Jared Day,[†] Surbhi Lal,[†] Peter Nordlander,[†,‡,*] and Naomi J. Halas[†,‡,*]

[†]Department of Electrical and Computer Engineering, [‡]Department of Physics and Astronomy, Laboratory for Nanophotonics, and the Rice Quantum Institute, Rice University, 6100 Main Street, Houston, Texas 77005, United States

ABSTRACT Solar illumination of broadly absorbing metal or carbon nanoparticles dispersed in a liquid produces vapor without the requirement of heating the fluid volume. When particles are dispersed in water at ambient temperature, energy is directed primarily to vaporization of water into steam, with a much smaller fraction resulting in heating of the fluid. Sunlight-illuminated particles can also drive H_2O—ethanol distillation, yielding fractions significantly richer in ethanol content than simple thermal distillation. These phenomena can also enable important compact solar applications such as sterilization of waste and surgical instruments in resource-poor locations.

KEYWORDS: plasmon · nanobubble · steam · distillation · photothermal

Solar energy has engendered extraordinary interest for its potential to provide power for a variety of processes without relying on fossil fuels.[1,2] While

these unusual nonequilibrium conditions, the water—ethanol azeotrope is breached and ethanol fractions approaching 99% are straightforwardly obtained.

Oara Neumann, Alexander S. Urban, Jared Day, Surbhi Lal, Peter Norlander, and Naomi J. Halas, "Solar Vapor Generation Enabled by Nanoparticles," *ACS namo,* 19 Nov. 2012.

Not Possible

FIG. 12. BALTIMORE AND OHIO RAILROAD LOCOMOTIVE, 4837, IDENTICAL IN DESIGN WITH THE ONE USED IN THE TESTS

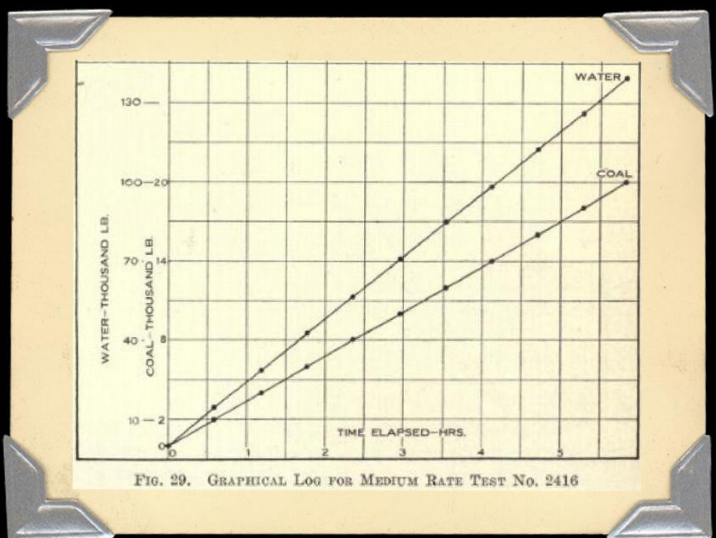
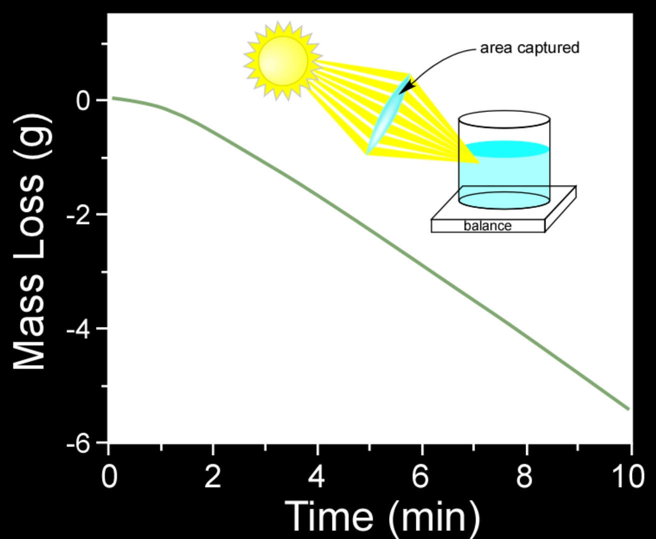


FIG. 29. GRAPHICAL LOG FOR MEDIUM RATE TEST No. 2416



Oara Neumann, Alexander S. Urban, Jared Day, Surbhi Lal, Peter Norlander, and Naomi J. Halas, "Solar Vapor Generation Enabled by Nanoparticles," *ACS namo,* 19 Nov. 2012.
Schmidt, Snodgras and Byer, Jr.; "Comparitive Tests of Six Sizes of Illionois Coal in a Mikado Locomotive", University of Illinois Engineering Experiment Station Bulletin No 101, September 1917.

What Consumers Invest In

Particularly Problematic in Biofuels

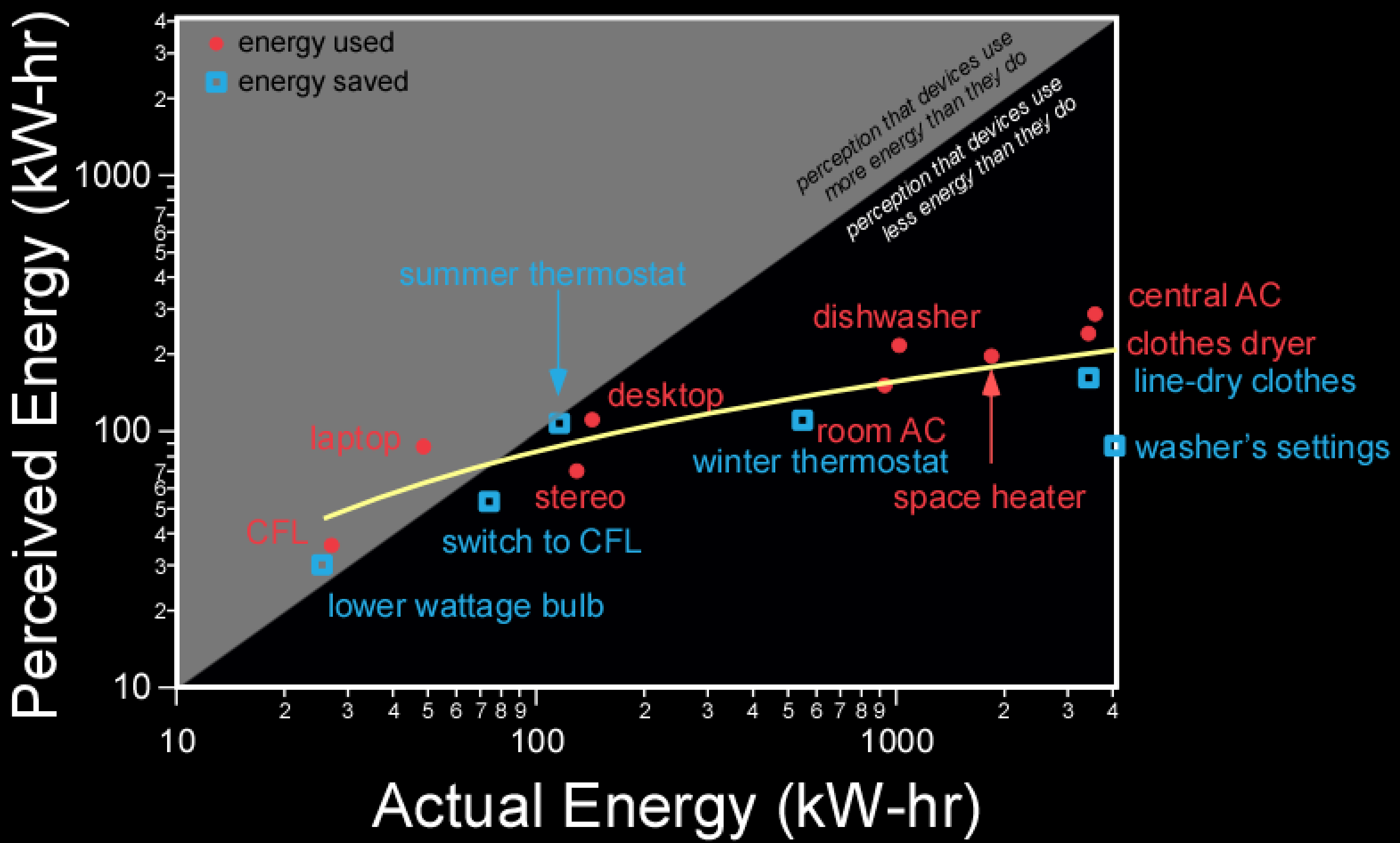
Hype

Practical Application

ENERGY DENSITY

LIMITATIONS OF BIOLOGY

We Are Poor Judges of the Energy We Use



We are poor judges of how much energy everyday devices consume.