Chemicals from Biomass:
Path to Perdition or the Promised Land?

Mark Jones

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Why does Truvia cost so much?

Cargill's Ms. McFerson says …. it costs more because it's more expensive to produce a plant-derived product. "We'll always be more expensive because rather than making something in one place, you're growing plants and working with farmers all through the supply chain," she says.

Chaker, Anne Marie; "Bracing for the Fake Sugar Rush", The Wall Street Journal, 4 January 2012, page D1.

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- How much *biomass is available?*
- How much *will the biomass cost?*
- How much *will biofuels cost?*
- How much *more are we willing to pay?*

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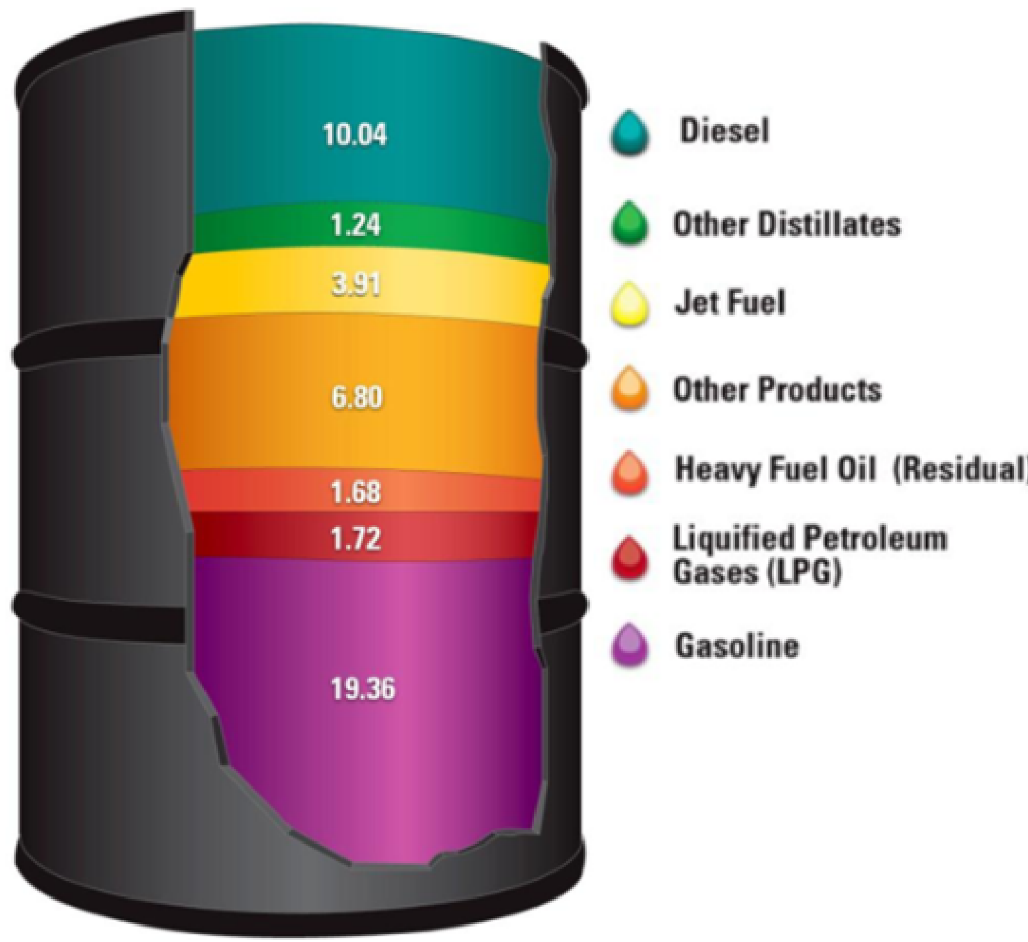
Biomass 2011: Replace the Whole Barrel, Supply the Whole Market

The New Horizons of Bioenergy

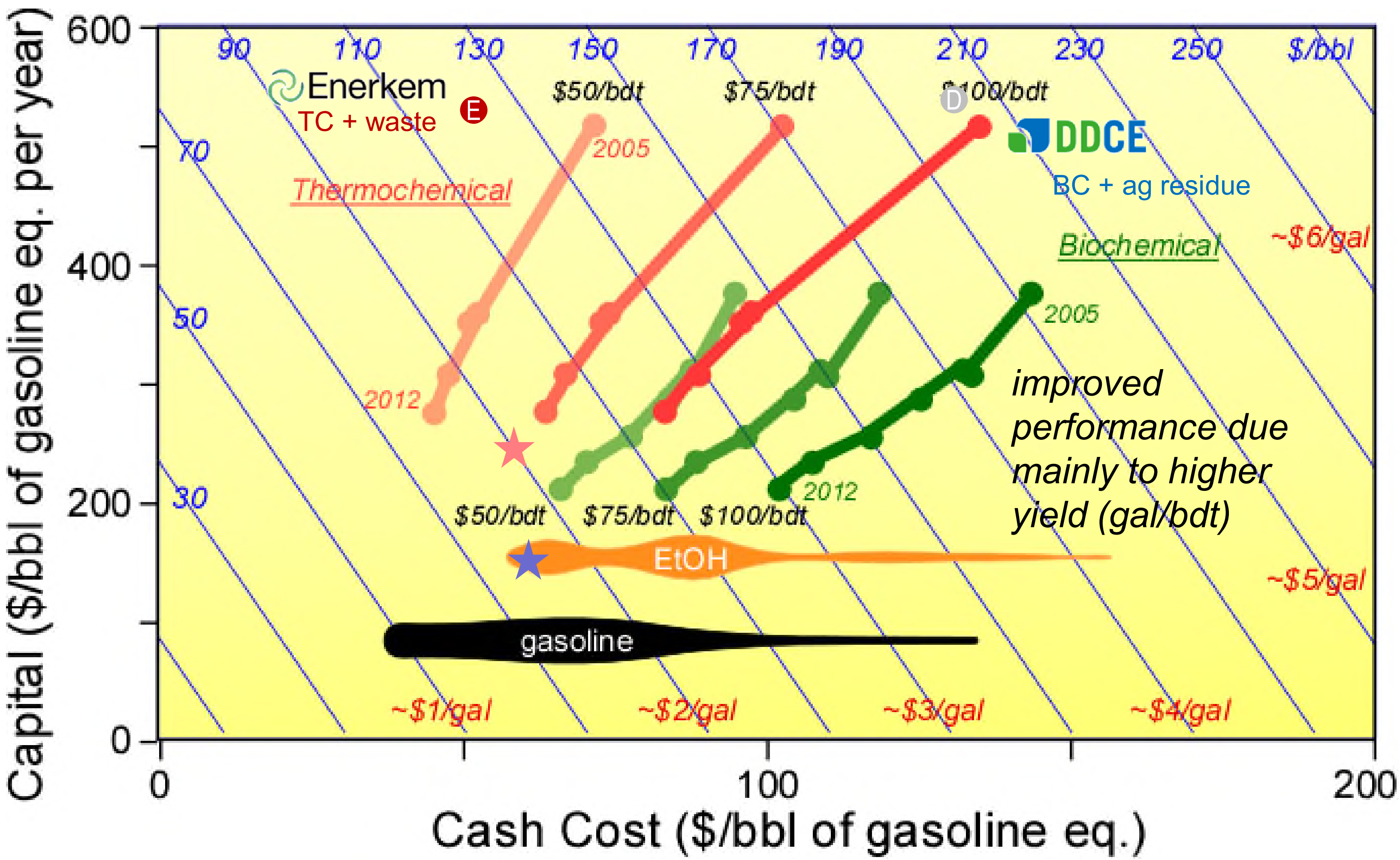
July 26–27, 2011

U.S. DEPARTMENT OF ENERGY BIOMASS 2011



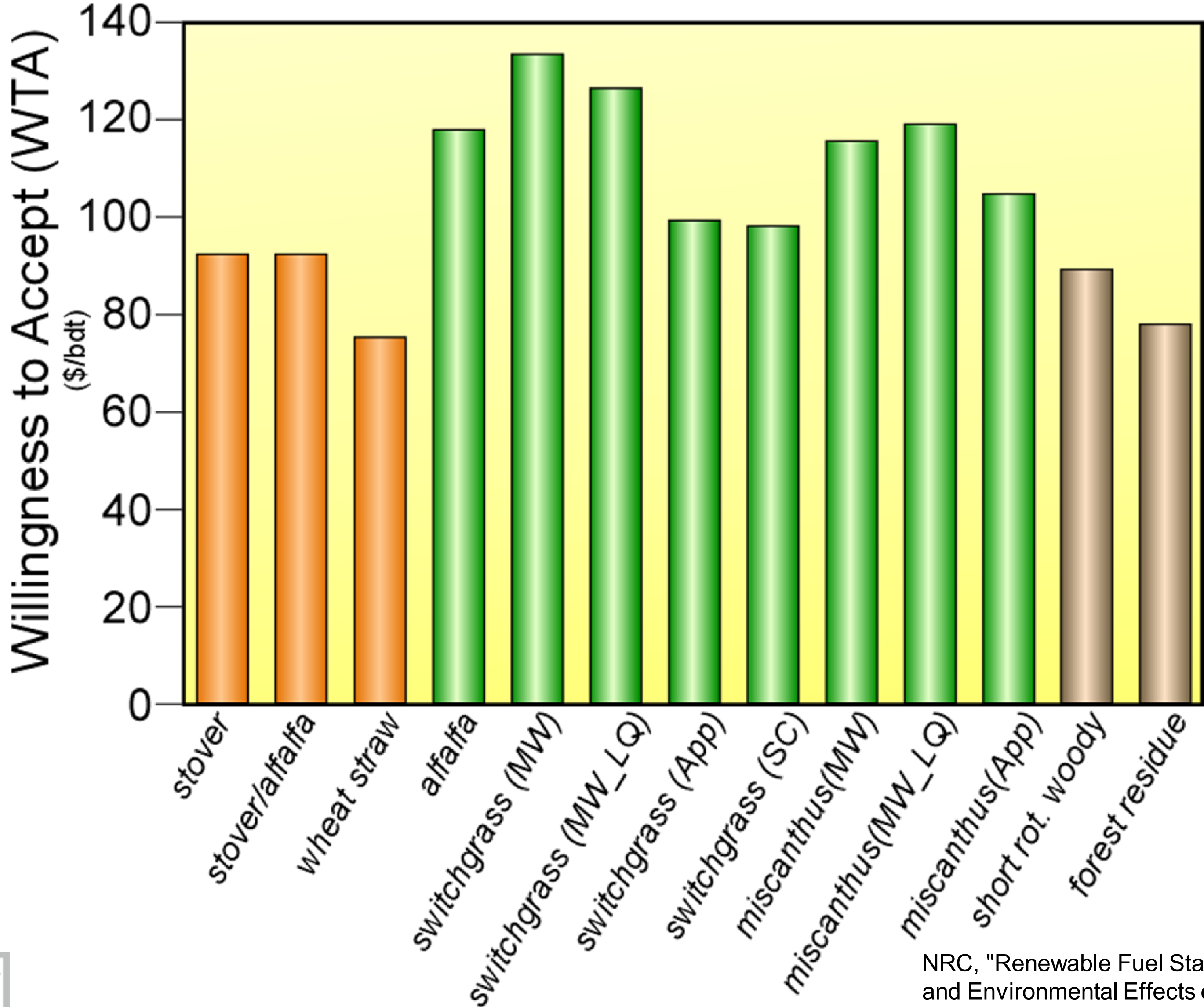
"sugar is the new crude"

DOE Cellulosic Fuels



Sources:
Crude Oil price, CMAI, Spot Average FOB price; monthly average prices from Jan 2005 to Jan 2011
Targets from DOE for Biochemical and Thermochemical routes; Capital from Biomass Multi Year Program 201 report from DOE (revisited by DOE on Nov 2010)
Corn Ethanol from the Center of Agricultural and Rural Development from Jan 2005 to Jan 2011

Biomass Cost



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

The hub of the biobased economy is of course the biorefinery – a dedicated facility for converting the sugars, oils and proteins from renewable biomass into multiple products such as biofuels, chemicals and materials such as plastics and polymers. The concept is modeled on the petroleum refinery, where petroleum is converted into fuels and chemicals that provide multiple product and revenue streams.

Just as a barrel of oil can be broken down into constituent parts that add up to more by volume and value than the original barrel, the objective of a biorefinery is to develop as many product and value streams as possible from biomass.

Brent Erickson
Executive Vice-President, BIO, Industrial and Environmental Section
Biofuels Digest, 6 January 2012

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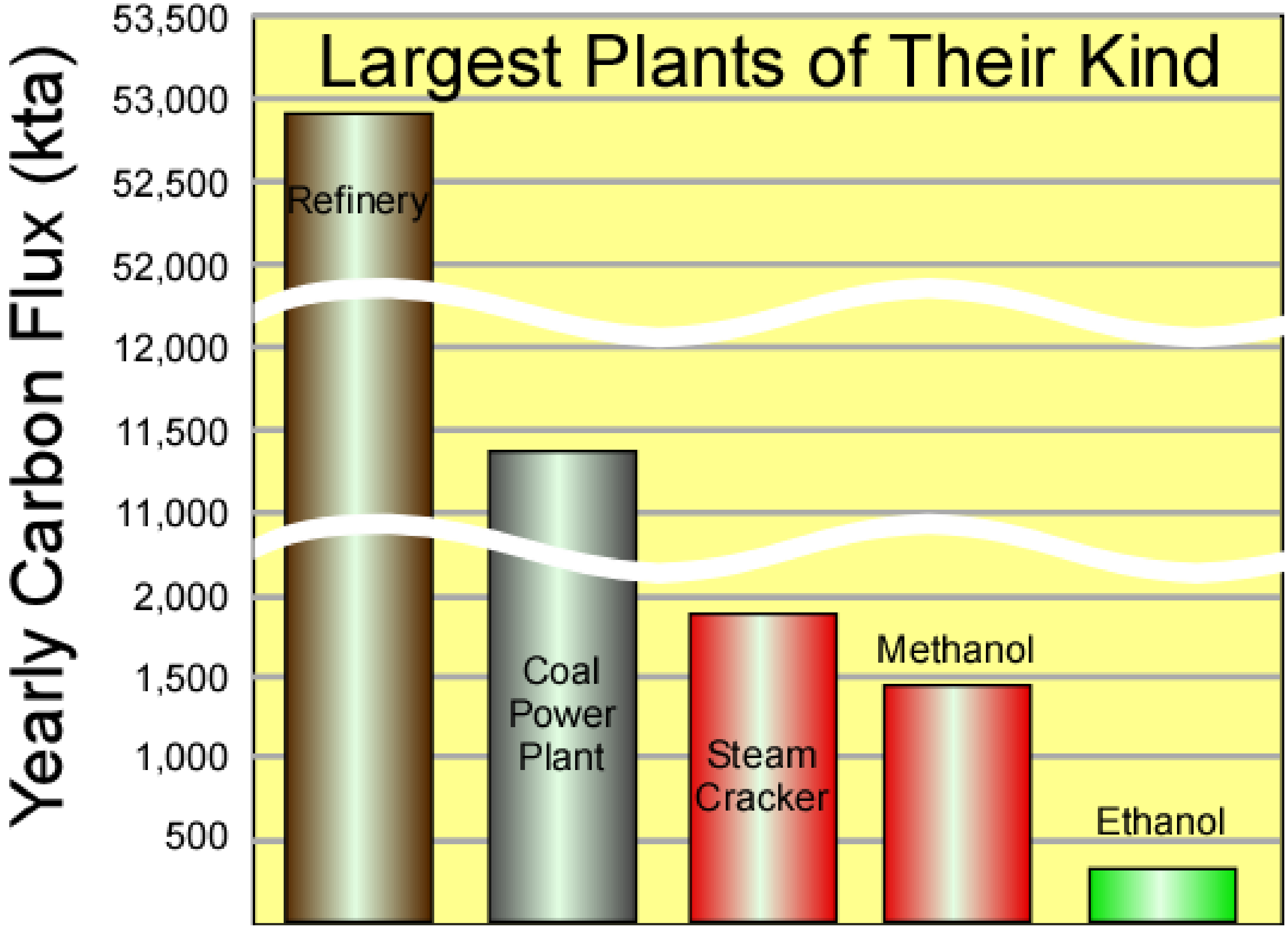
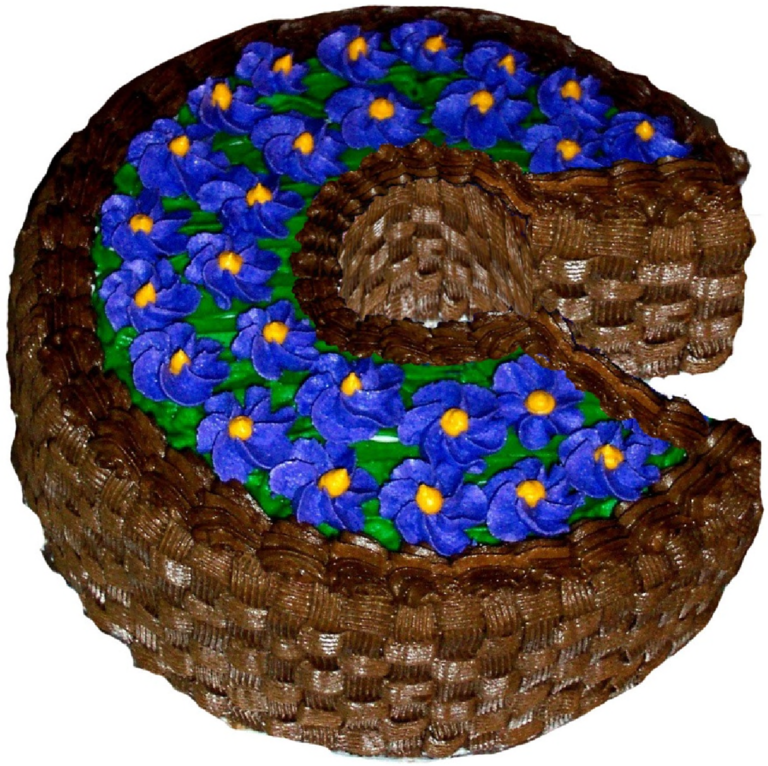


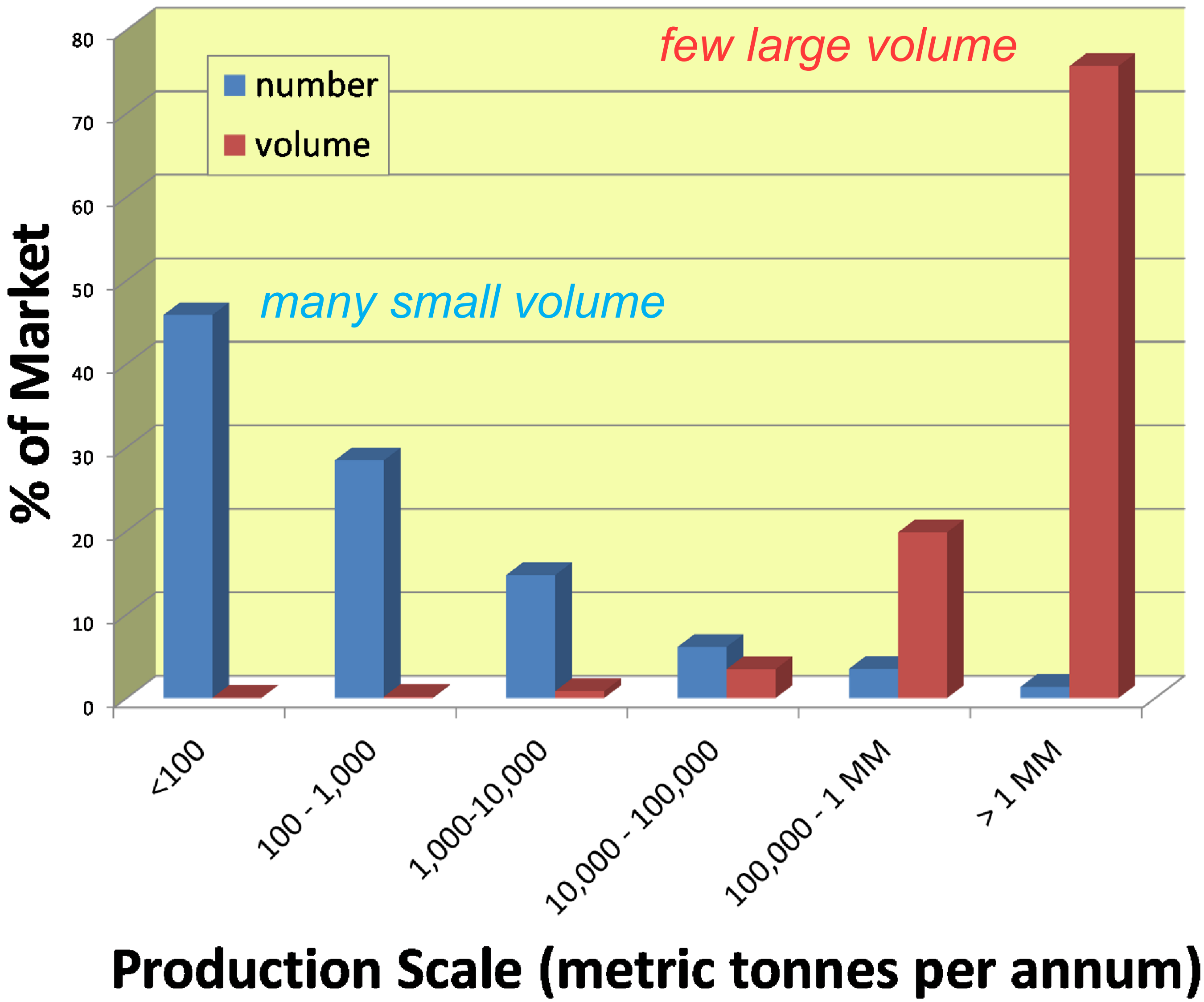
feedstock limits scale

Chemical Industry Overview

- consider only the industry sells *decorated carbon*

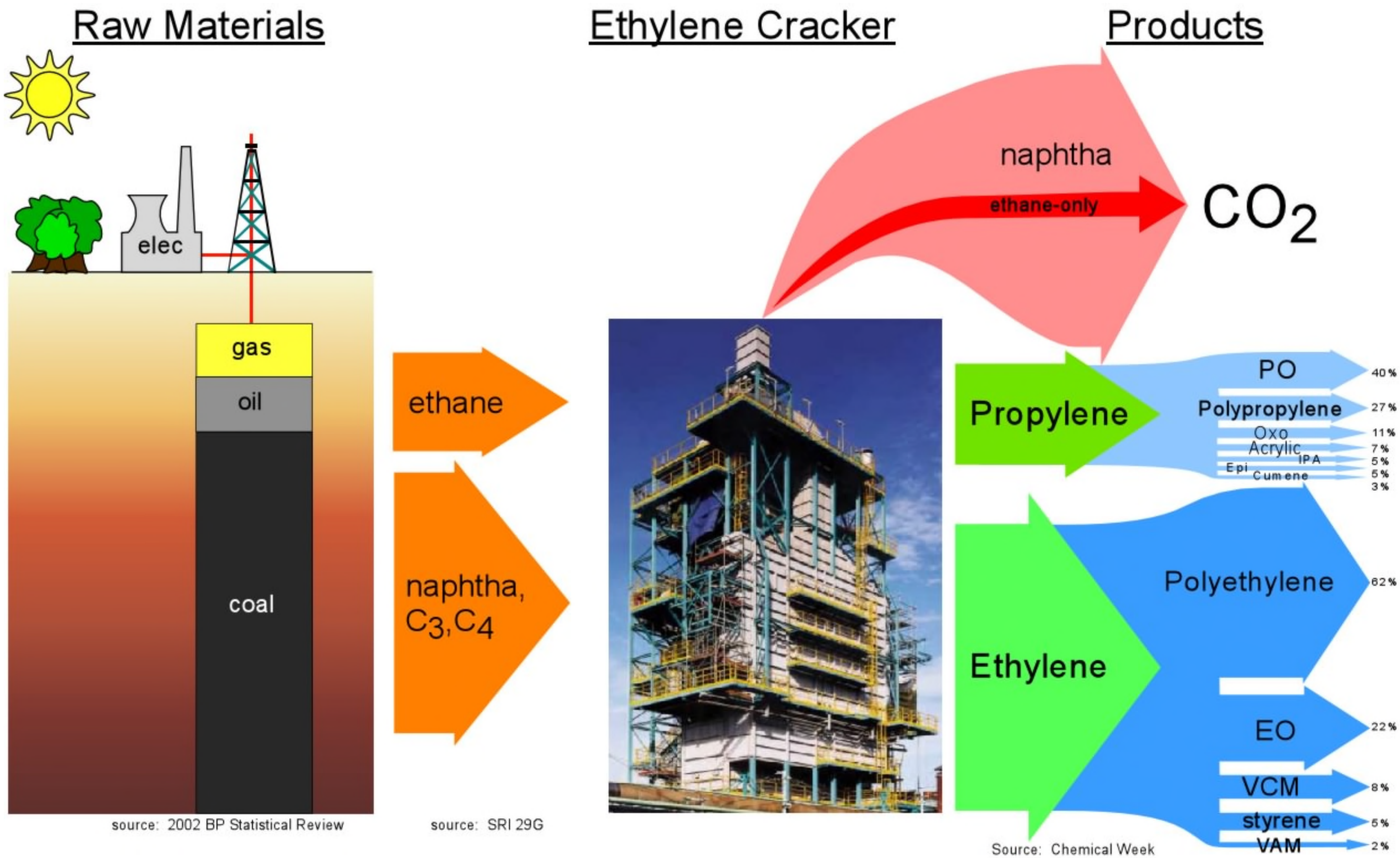


Chemical Industry



data for Europe from OECD; "Environmental Outlook for the Chemicals Industry", 2001.

Chemical Industry



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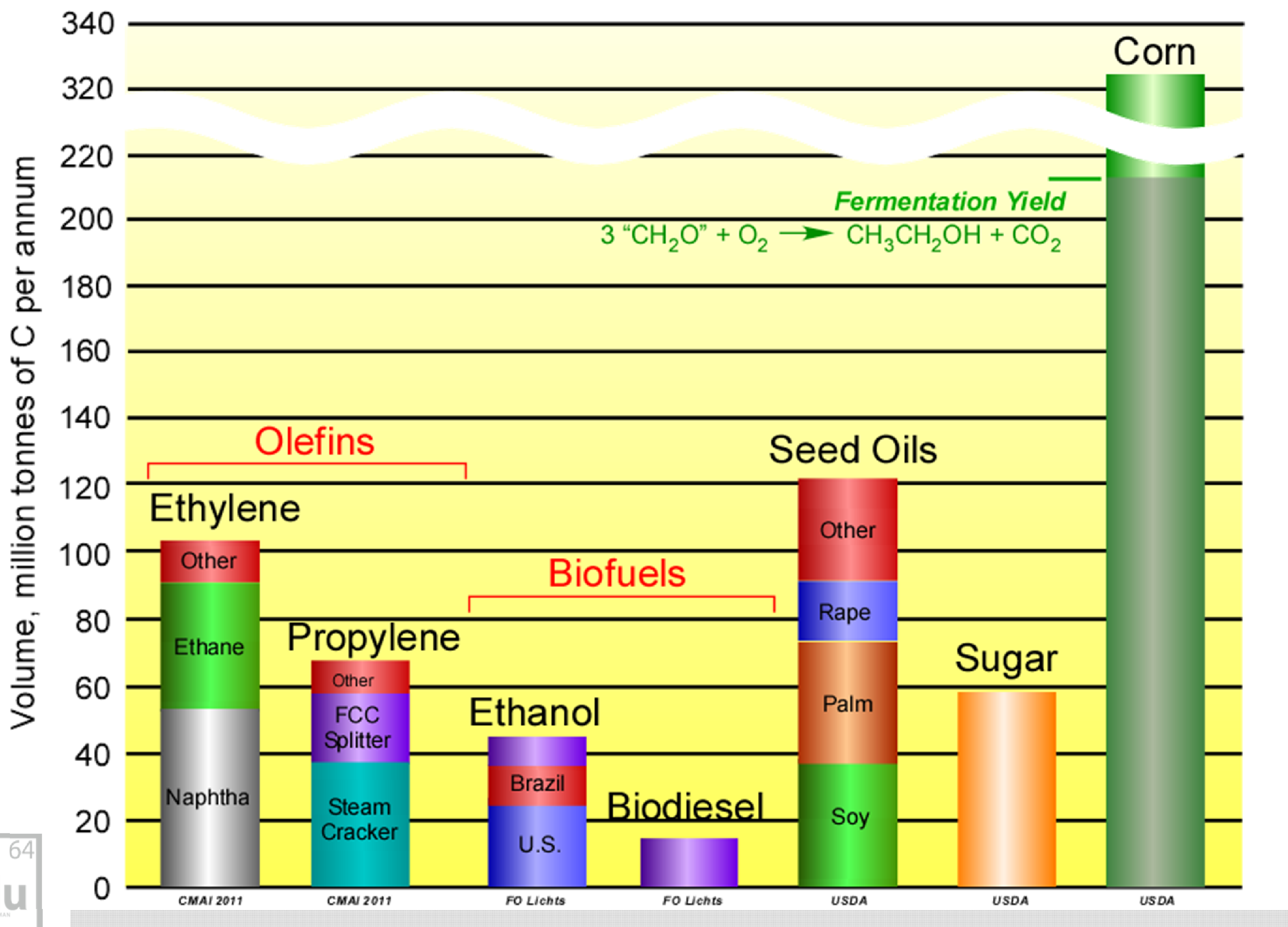
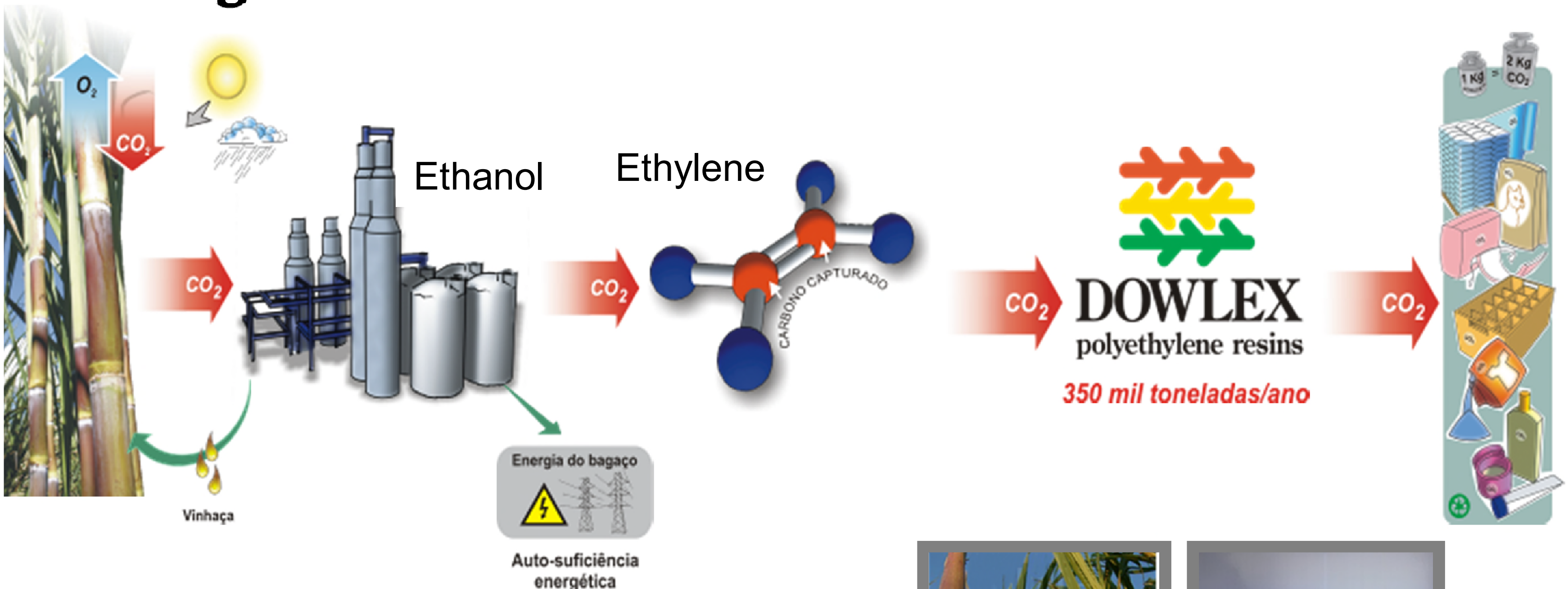
R.I.P.
U.S.
Chemical
Industry
1776-2008

Global Commodity Production



Making Chemicals from Biomass- Cane to LLDPE



Fully-integrated facility in Brazil
Utilizes state-of-the-art Dow polymerization catalysis

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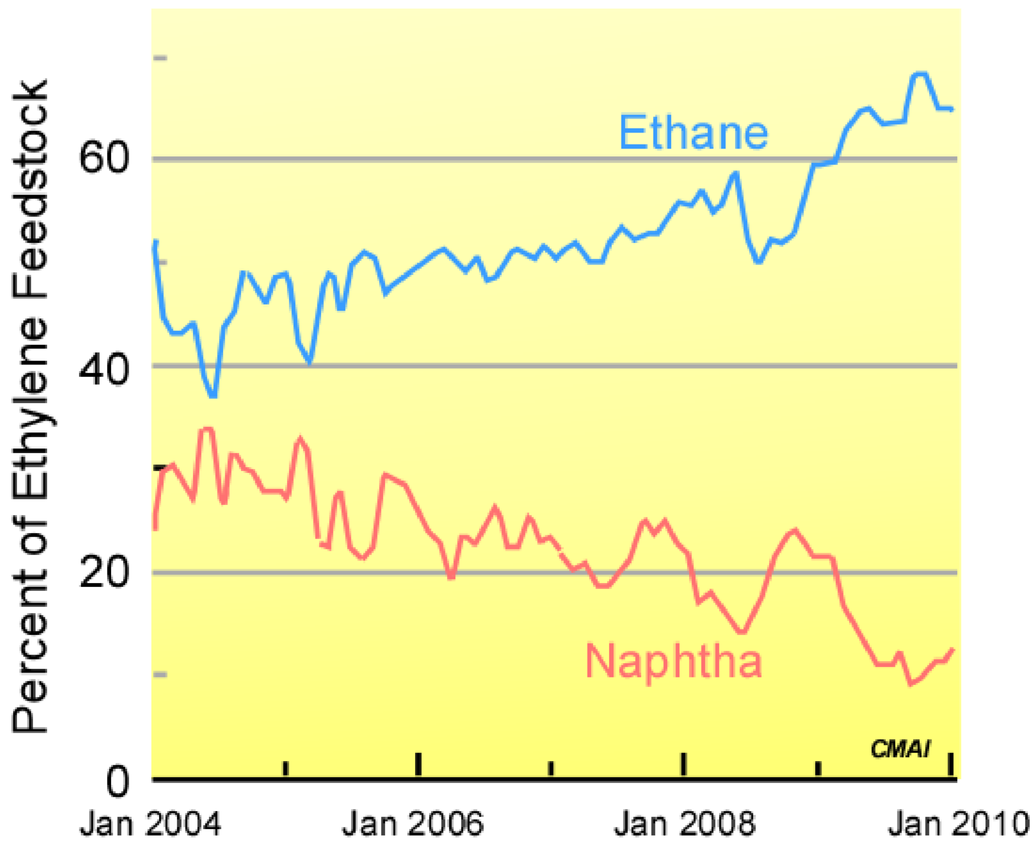
Shale Gas Revitalizes the Industry



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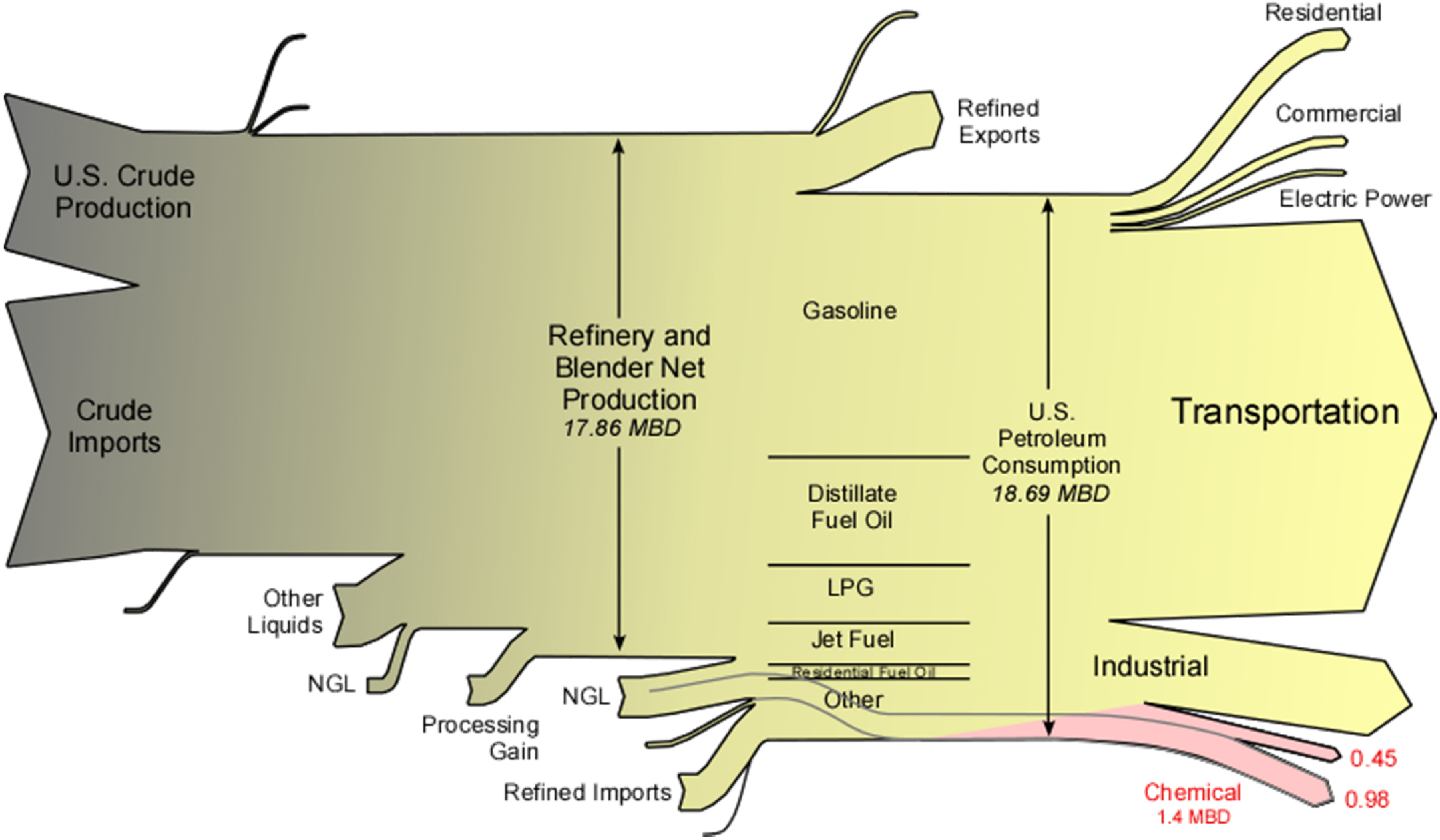
Petroleum Flow 2009



EIA, "Annual Energy Review 2009", August 2010, DOE/EIA-0384(2009) and Sean Davis, "SRI Petroleum Liquid Feedstocks", June 2010

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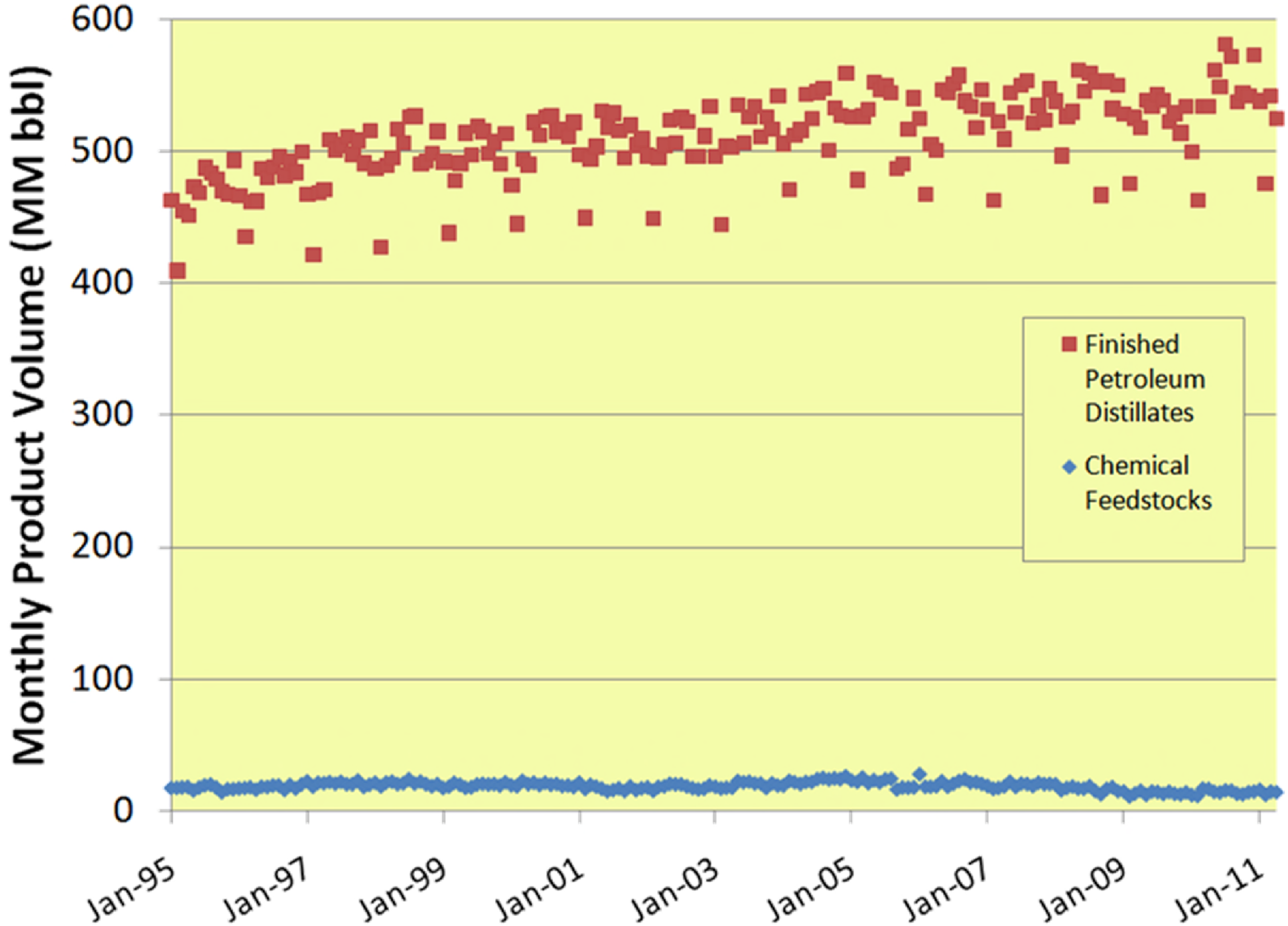
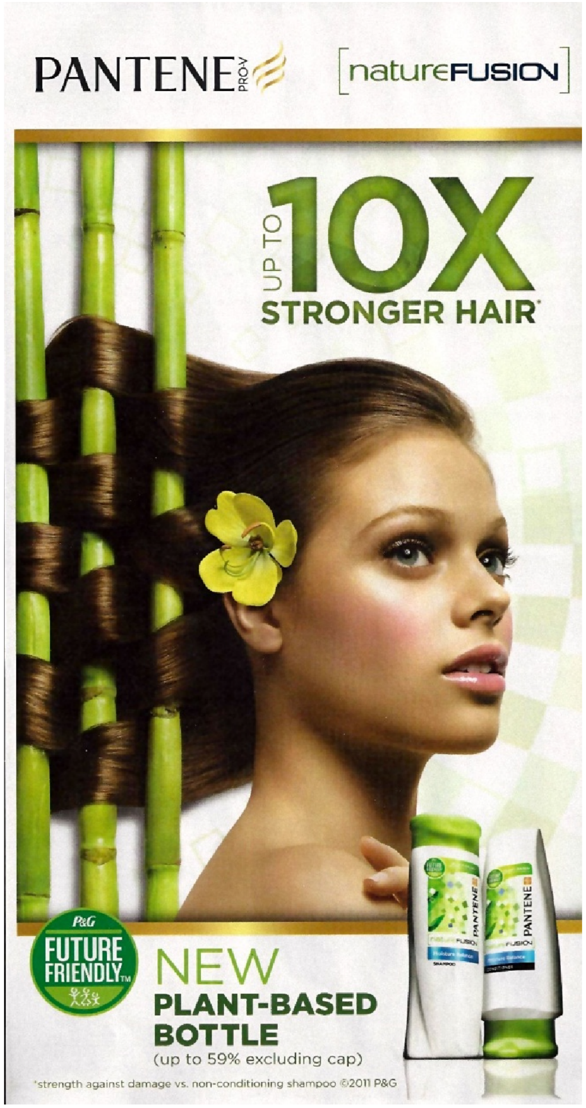
Feedstock Flows from Petroleum



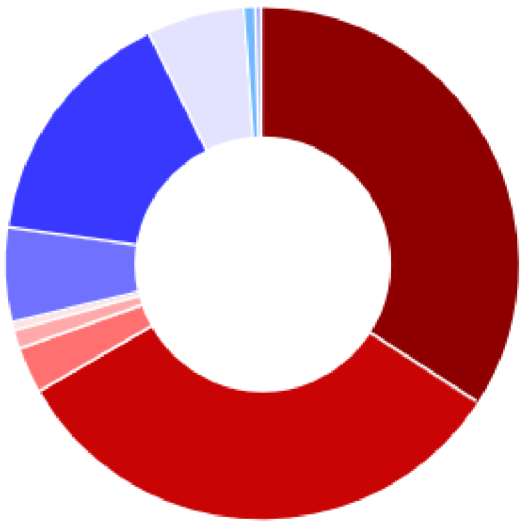


Midland Daily News

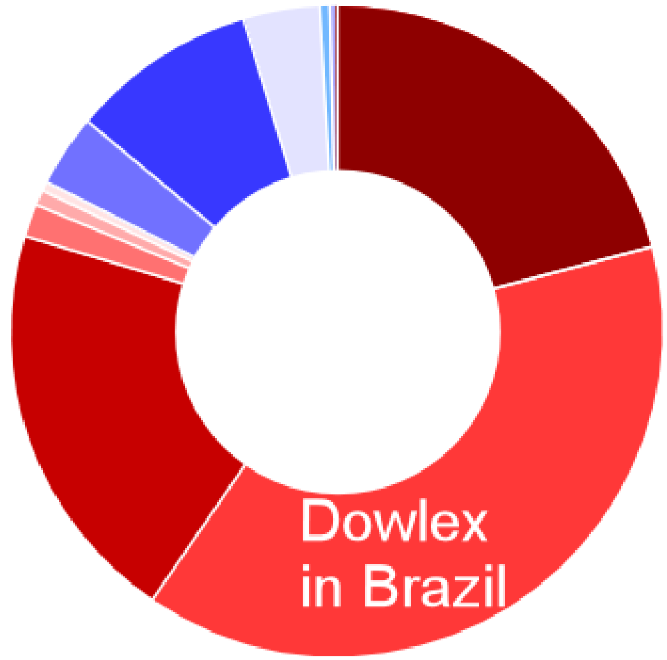
1 January 2012

Bioplastics

Current



with Brazil Dowlex



	Current tpa	Current %	with Bzl LLDPE tpa	with Bzl LLDPE %
PLA	207002	34.0	207002	21.6
Bzl LLDPE	-	-	350000	36.5
Bio-PE	200000	32.8	200000	20.8
PLA blends	18000	3.0	18000	1.9
cellulose der.	8000	1.3	8000	0.8
bio-urethanes	2720	0.4	2720	0.3

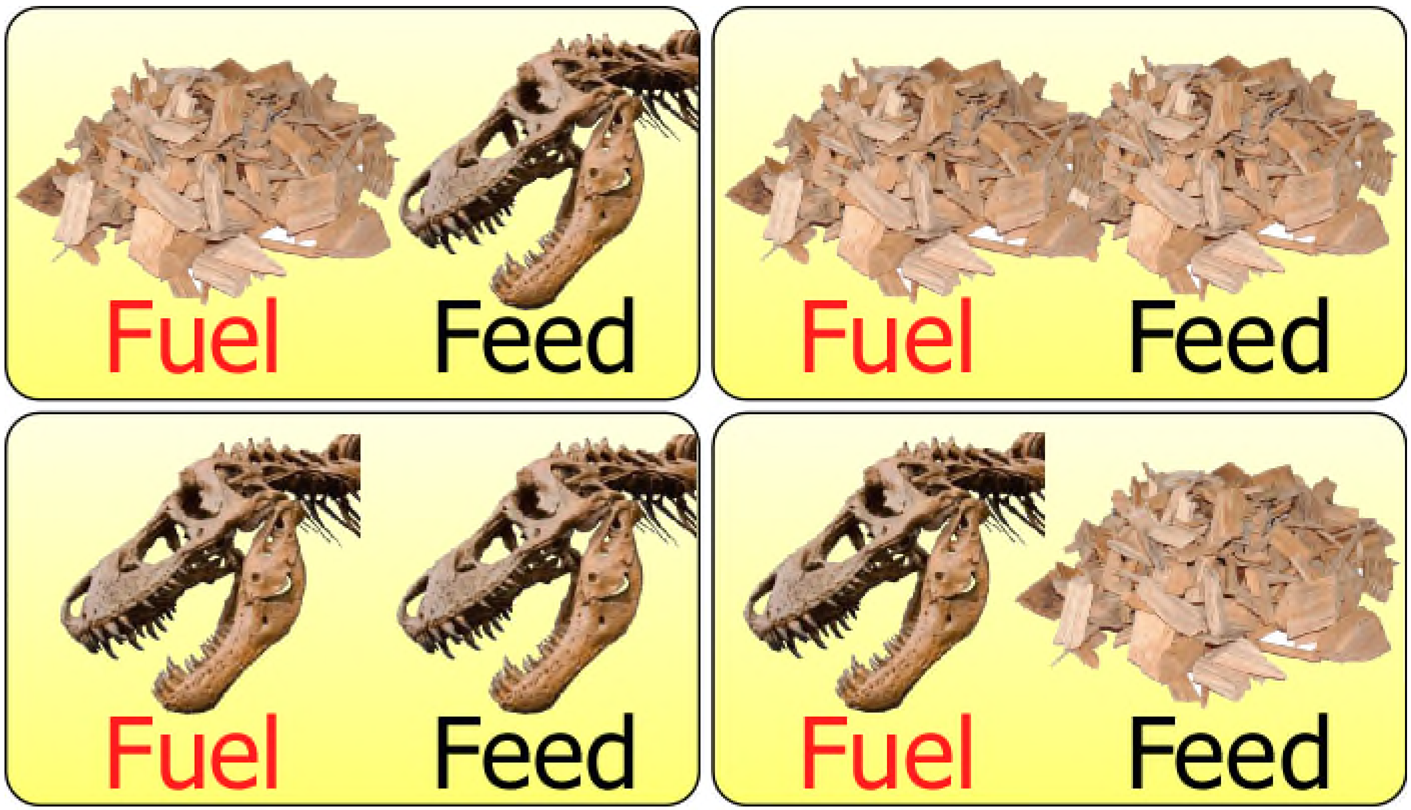
	Current tpa	Current %	with Bzl LLDPE tpa	with Bzl LLDPE %
regen cellulose	36000	5.9	36000	3.8
PHA	93051	15.3	93051	9.7
bio-polyamides	36500	6.0	36500	3.7
starch blends	5075	0.8	5075	0.5
bio-TPE +	3000	0.5	3000	0.3
Bio-PC	300	0.0	300	0.0

European Bioplastics, "Driving the Evolution of Plastics", April 2011

Twelve Principles of Green Chemistry

1. Prevention: It is better to prevent waste than to treat or clean up waste after it has been created.
2. Atom Economy: Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Less Hazardous Chemical Syntheses: Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Designing Safer Chemicals: Chemical products should be designed to effect their desired function while minimizing their toxicity.
5. Safer Solvents and Auxiliaries: The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. Design for Energy Efficiency: Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. Use of Renewable Feedstocks: A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. Reduce Derivatives: Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. Catalysis: Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Design for Degradation: Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. Real-time analysis for Pollution Prevention: Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Inherently Safer Chemistry for Accident Prevention: Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Two Carbon Flavors

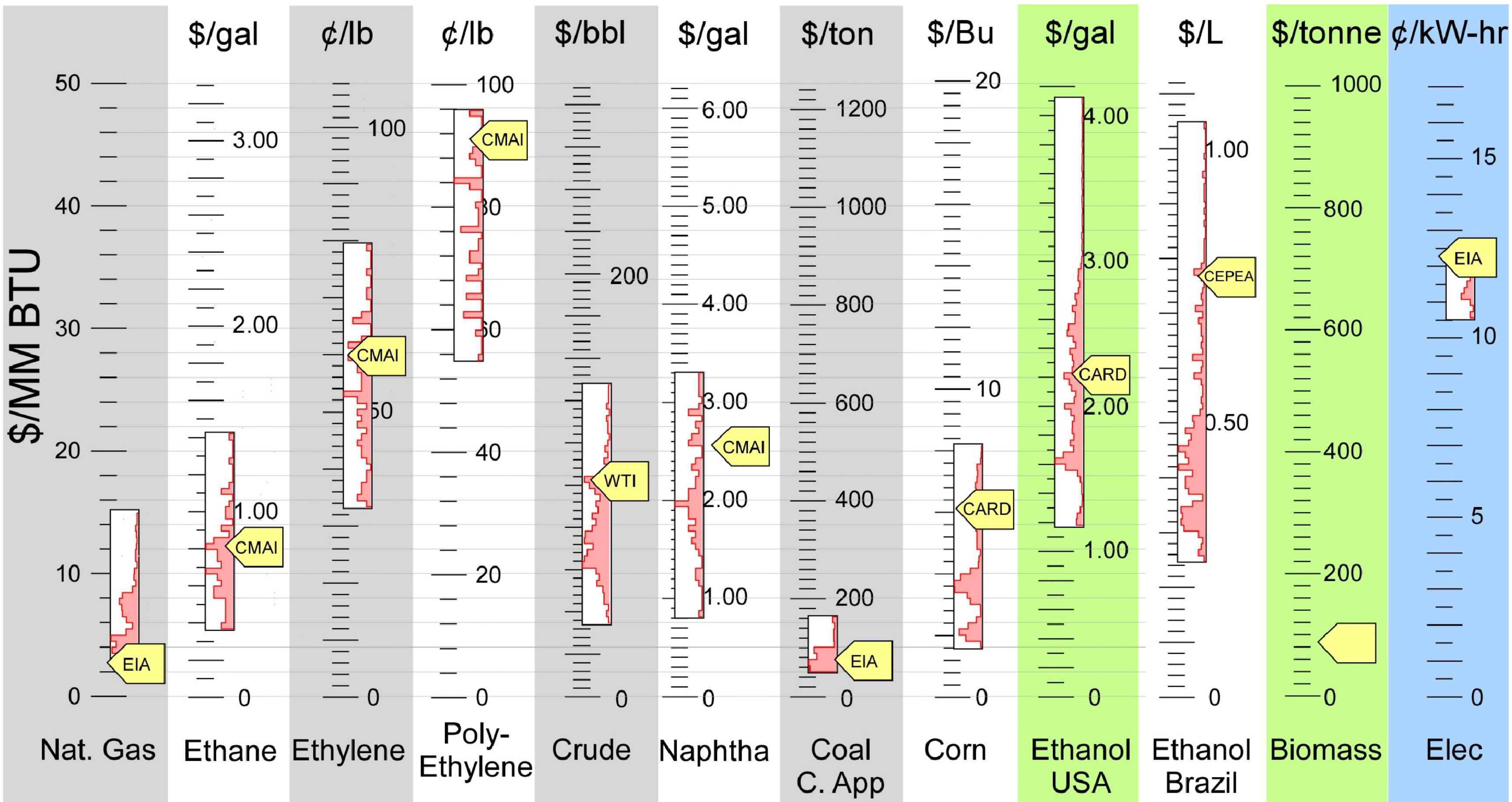


LCA of Polymers

Biopolymers rank in the middle of LCA rankings

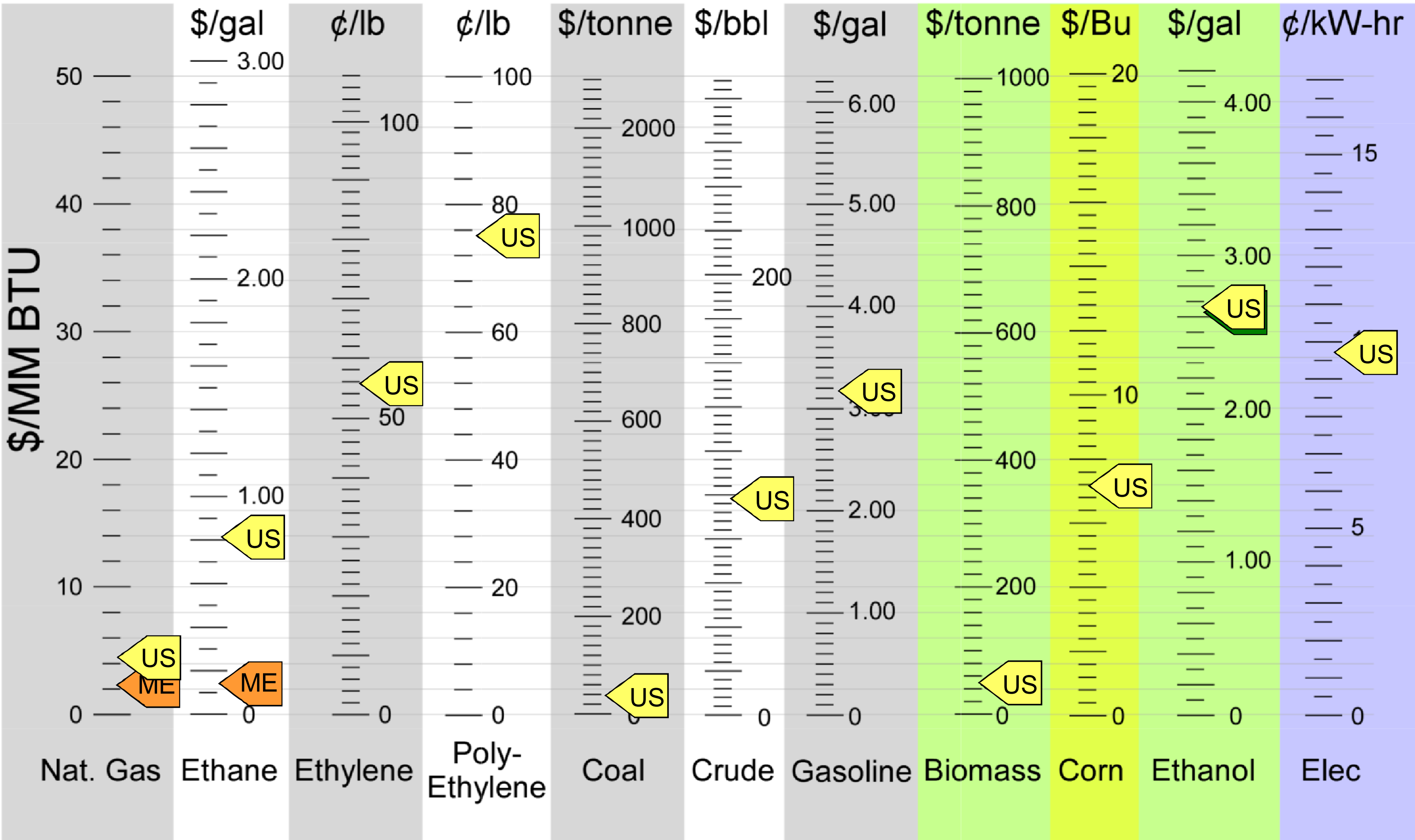
POLYMER	Material	Green Design Rank	LCA Rank
Polylactic Acid – NatureWorks	Sugar/cornstarch	1	6
Polyhydroxyalkanoate-Stover	Cornstalks	2	4
Polyhydroxyalkanoate-General	Corn kernels	2	8
Polylactic Acid -General	Sugar/cornstarch	4	9
HD Polyethylene	Petroleum	5	2
PET	Petroleum	6	10
LD Polyethylene	Petroleum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

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

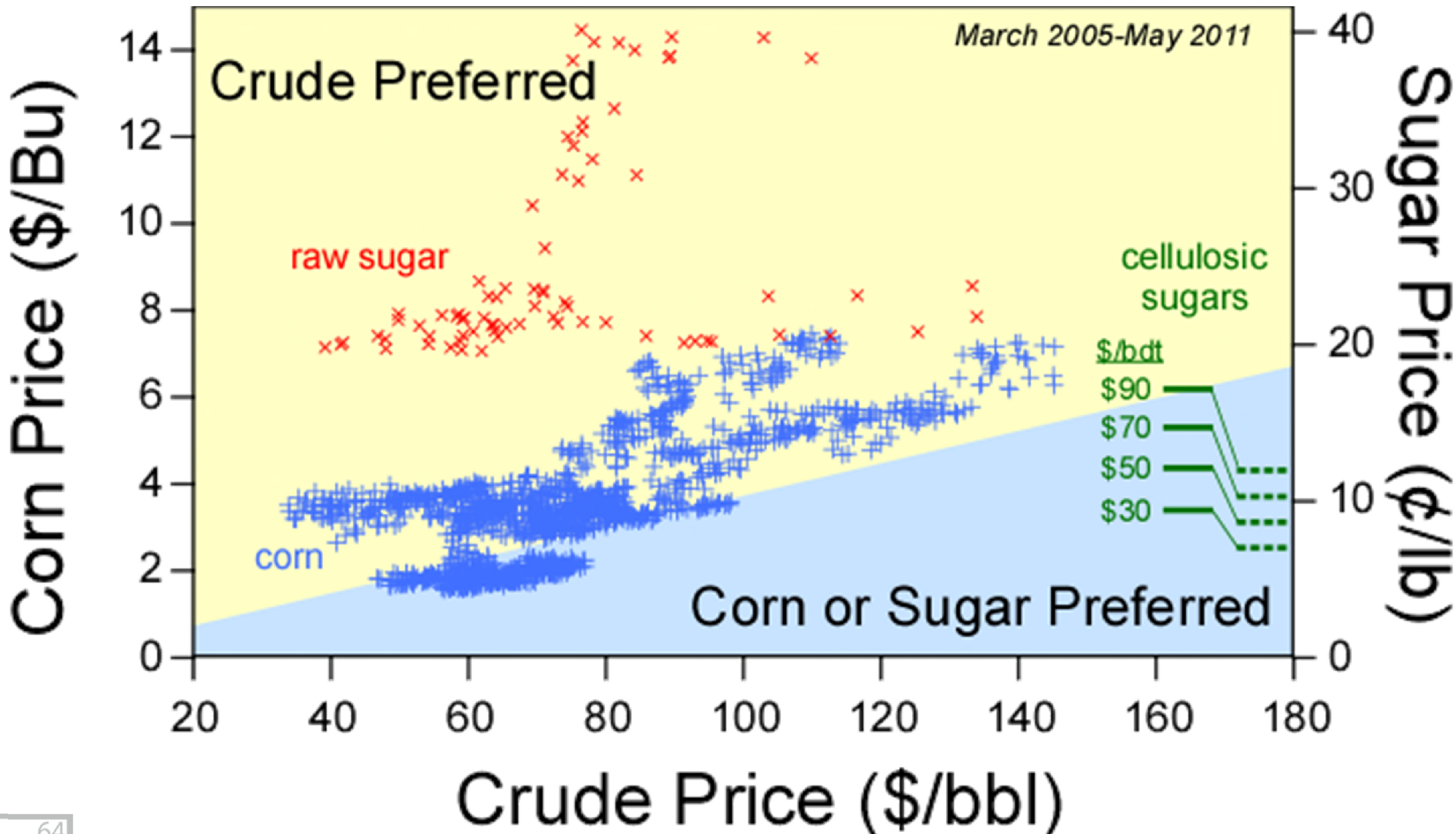


$/MM BTU
$/gal
¢/lb
¢/lb
$/bbl
$/gal
$/ton
$/Bu
$/gal
$/L
$/tonne
¢/kW-hr
EIA
CMAI
CMAI
CMAI
WTI
CMAI
EIA
CARD
CARD
CEPEA
EIA
Nat. Gas
Ethane
Ethylene
Poly-Ethylene
Crude
Naphtha
Coal C. App
Corn
Ethanol USA
Ethanol Brazil
Biomass
Elec

Feedstocks are Energy

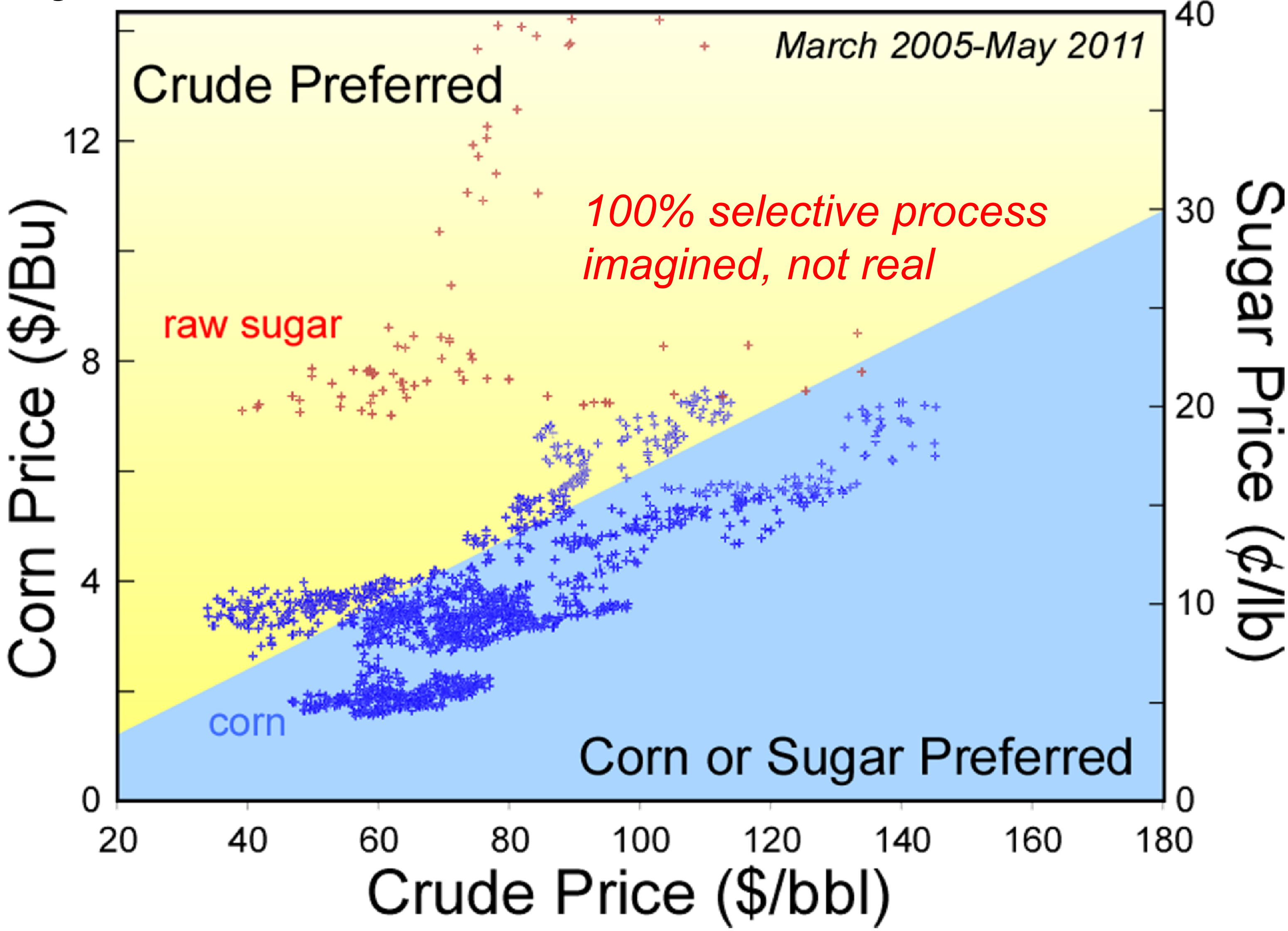


Ethylene Raw Material Cost – *Fossil or Bio?*



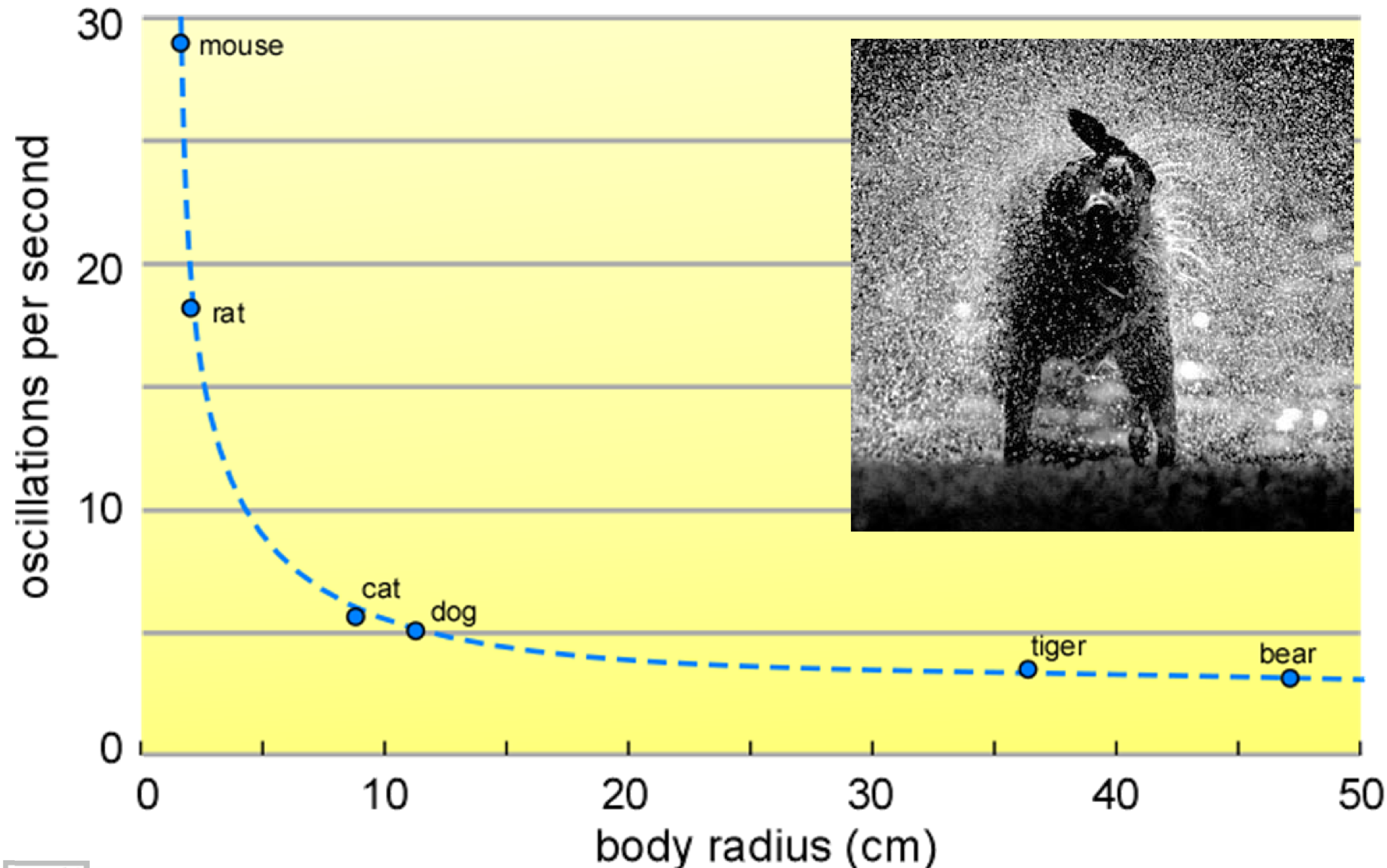
modeled after Chemical Marketing Resources (cmrhoutex.com)

p-Xylene Raw Material Cost



modeled after Chemical Marketing Resources (cmrhoutex.com)

Interesting Correlation



Andrew Dickerson, Grant Mills, Jay Bauman, Young-Hui Chang, David Hu, The Wet-Dog Shake, Fluid Dynamics, 15 October 2010.

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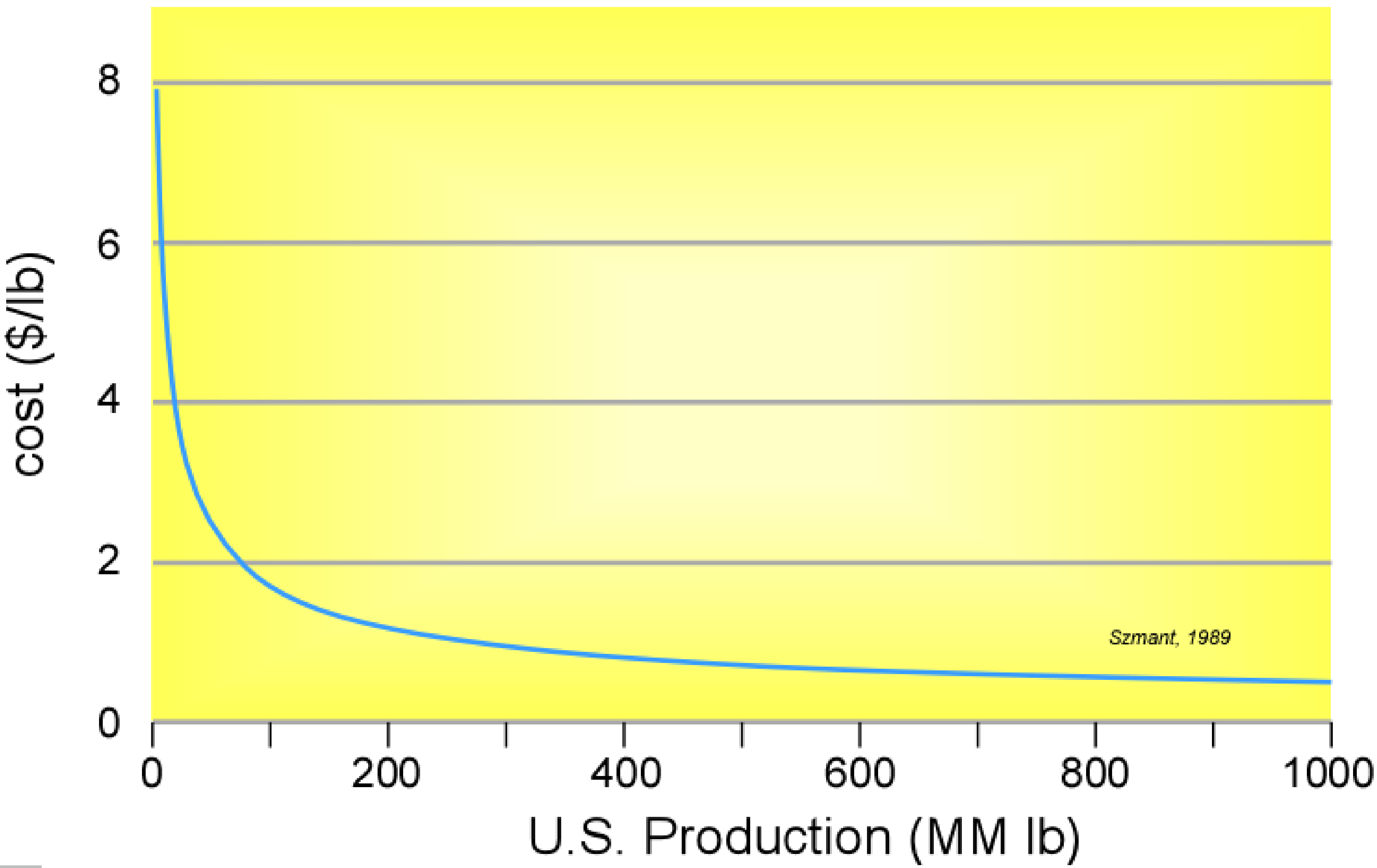
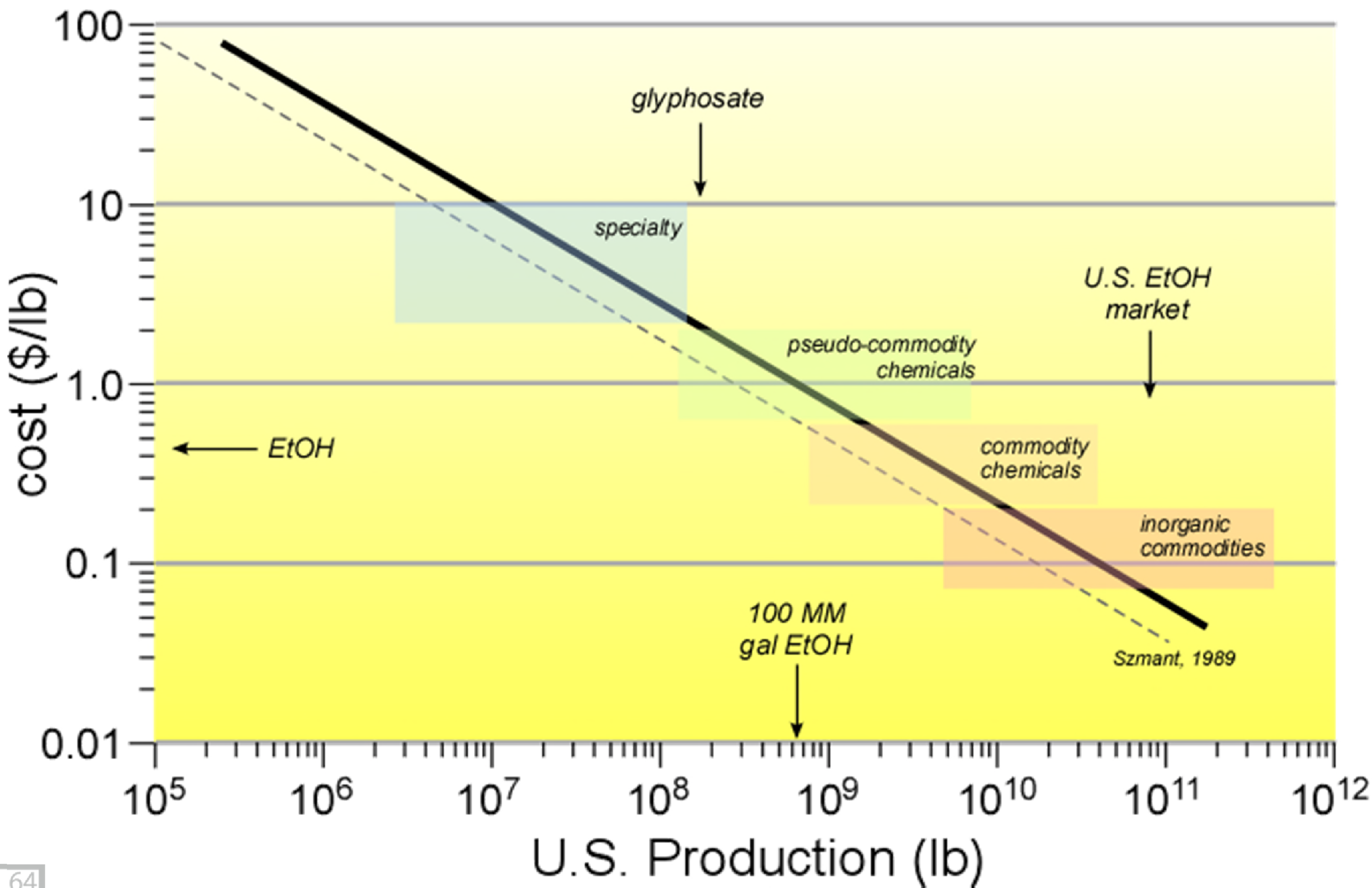
Scale Matters!



Most Common Version



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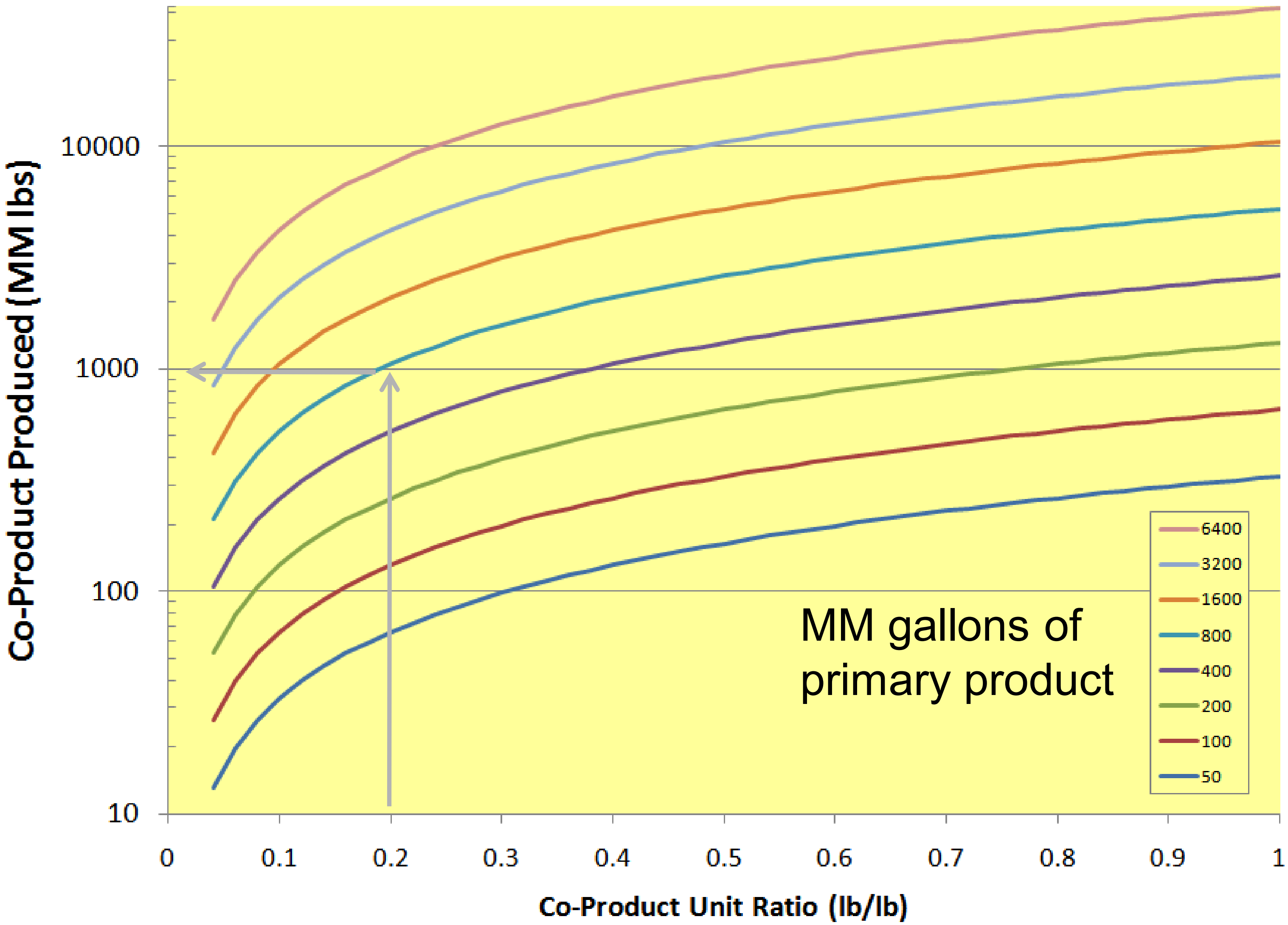
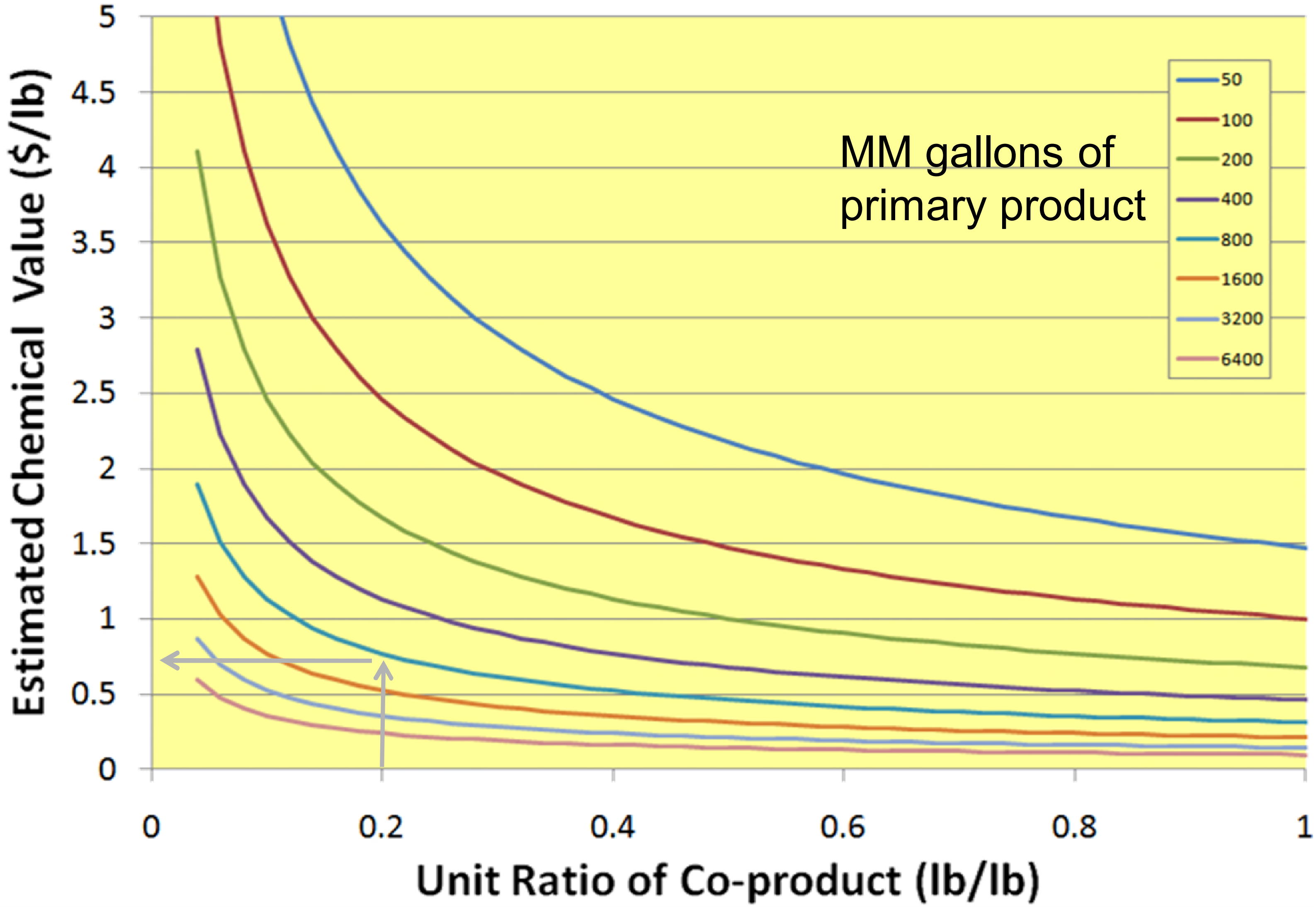
Implications

20% coproduct at 800 MM gallons is 1 B lbs



More Implications

20% coproduct at 800 MM gallons is ~$0.75/lb



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What works in bioproducts?

- nature prepares the molecule:
  - nature puts it in the right oxidation state (*kind of carbon*)
  - nature makes the right molecular structure for the end application(*shape of carbon*)
  - nature makes enough that recovery is economical
- technical risk to serve market is low
  - identical biomaterial for established markets
  - fossil and bio parity in market

Using sunlight, CO_2 and little else, many varieties of fast-growing pond scum, when starved of nutrients, quickly build up oil in their cells. They need no external sugar from corn or cane to grow, so they don't compete with food crops. Farmed in ponds or translucent reactors, microalgae can be raised on cheap, sun-splashed land that is unsuitable for crops or much of anything else.

Voosen, Paul; "As Algae Bloom Fades, Photosynthesis Hopes Still Shine", New York Times, 29 March 2011.

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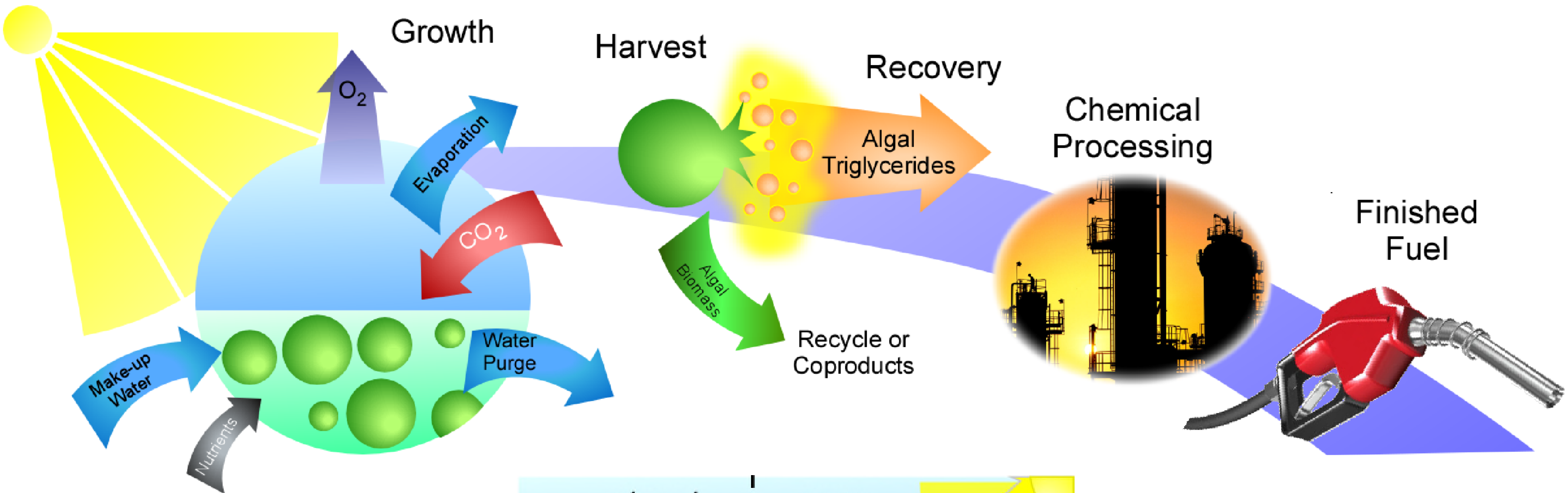
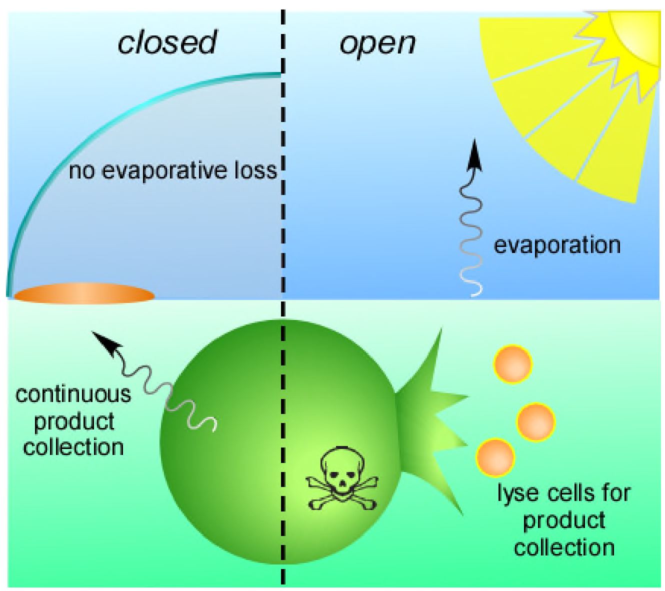
Algae – hype or real?





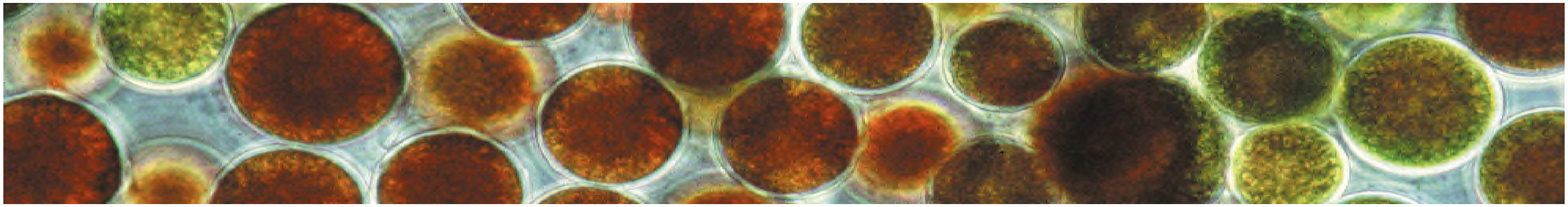


Table 1
Comparison of some sources of biodiesel

Crop	Oil yield (L/ha)	Land area needed (M ha)[a]	Percent of existing US cropping area[a]
Corn	172	1540	846
Soybean	446	594	326
Canola	1190	223	122
Jatropha	1892	140	77
Coconut	2689	99	54
Oil palm	5950	45	24
Microalgae[b]	136,900	2	1.1
Microalgae[c]	58,700	4.5	2.5

[a] For meeting 50% of all transport fuel needs of the United States.
[b] 70% oil (by wt) in biomass.
[c] 30% oil (by wt) in biomass.

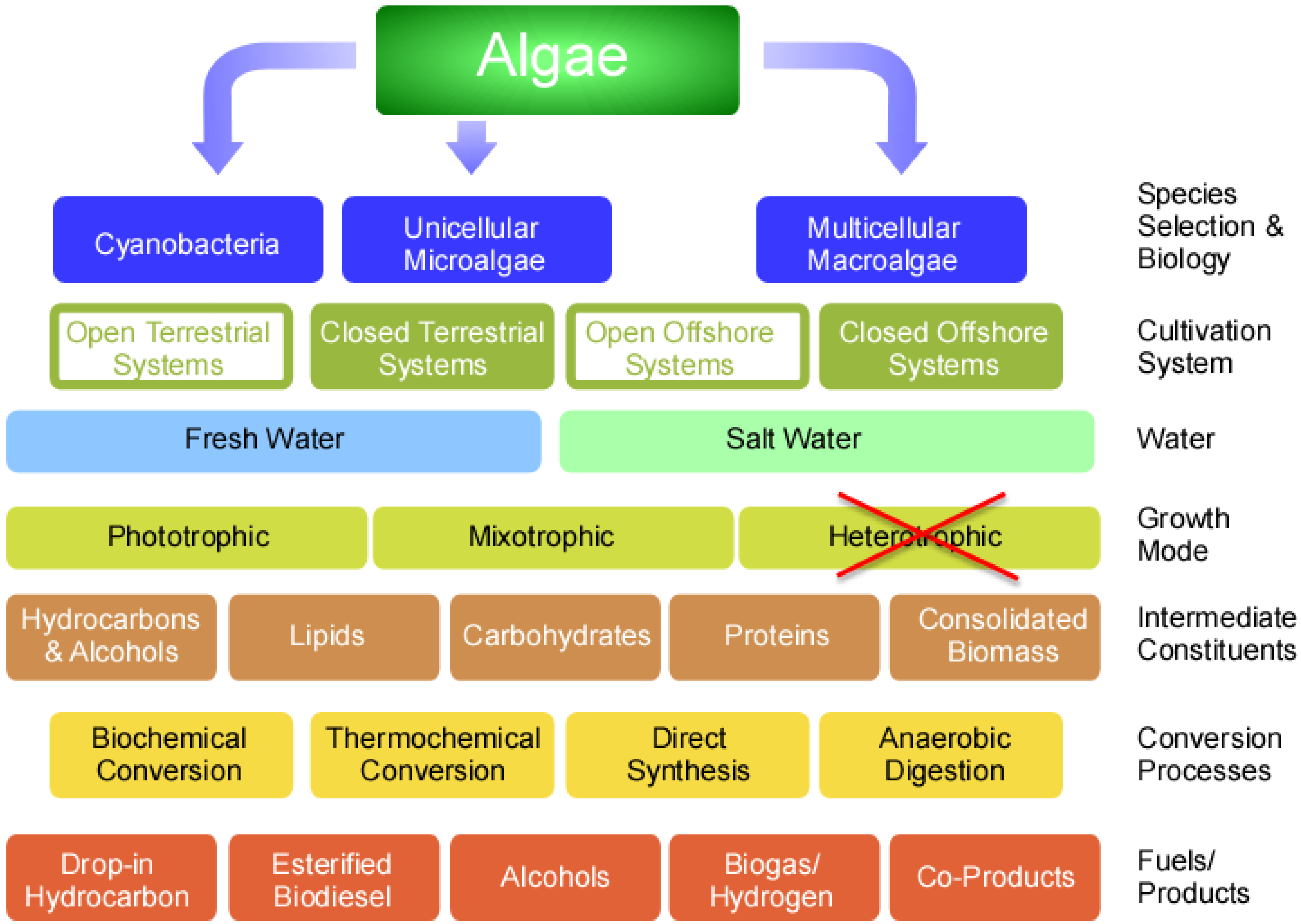
That chart perpetuates one of the biggest myths out there. Everybody has seen versions of that chart. [But] I've never seen what I'd say to be proof that algae has even made as much oil as soybeans.

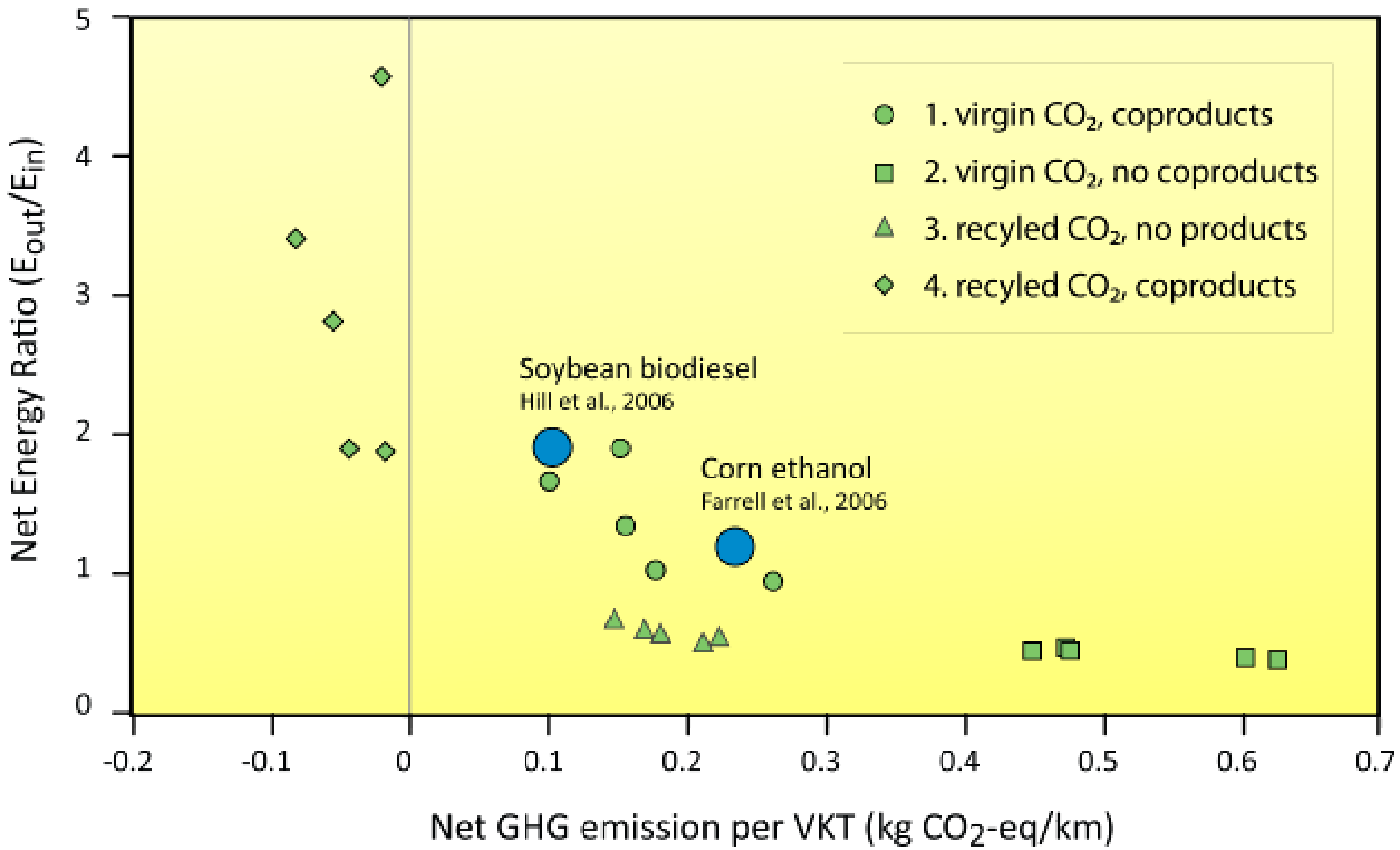
Harrison Dillon
CEO, Solazyme

Yusef Chisti, "Biodiesel from Microalgae", *Biotechnology Advances* **25** (2007), 294-306.

Voosen, Paul; "As Algae Bloom Fades, Photosynthesis Hopes Still Shine", New York Times, 29 March 2011.

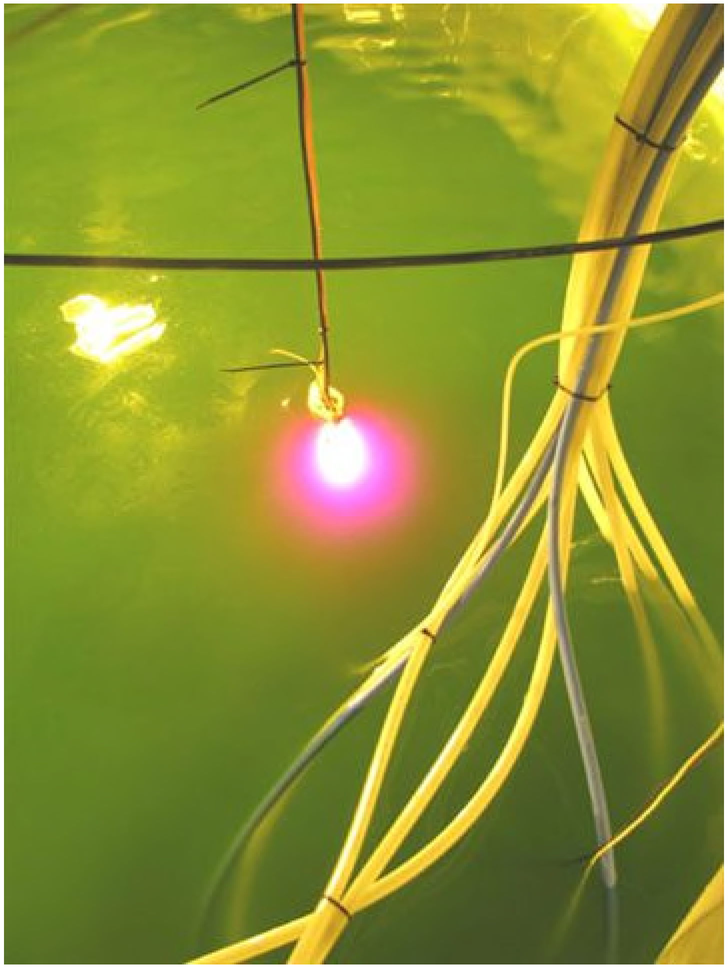
Lots of possibilities





Liu, Xiaowei; Clarens, Andres F.; Colosi, Lisa M.; "Algae biodiesel has potential despite inconclusive results to date", *Bioresource Technology*, Volume 104, January 2012, Pages 803

Practical?

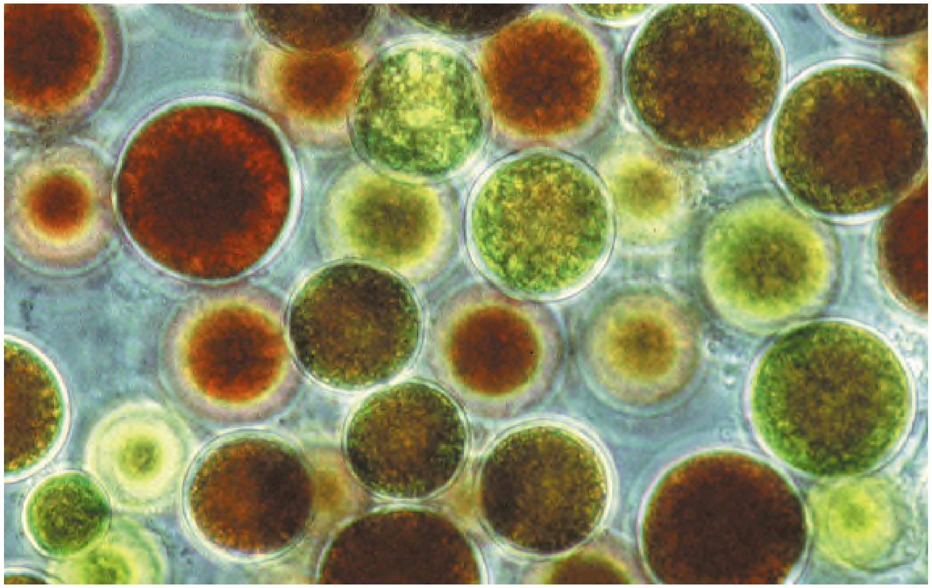


LumiGrow LED technology is instrumental to the operation of Algae Farm's algae biomass production system, which will produce algae for the nutraceutical, cosmetic and *renewable energy market sectors*. By growing in a climate-controlled indoor environment, Algae Farm can achieve predictable and scalable yields while it maintains the highest purity standards.

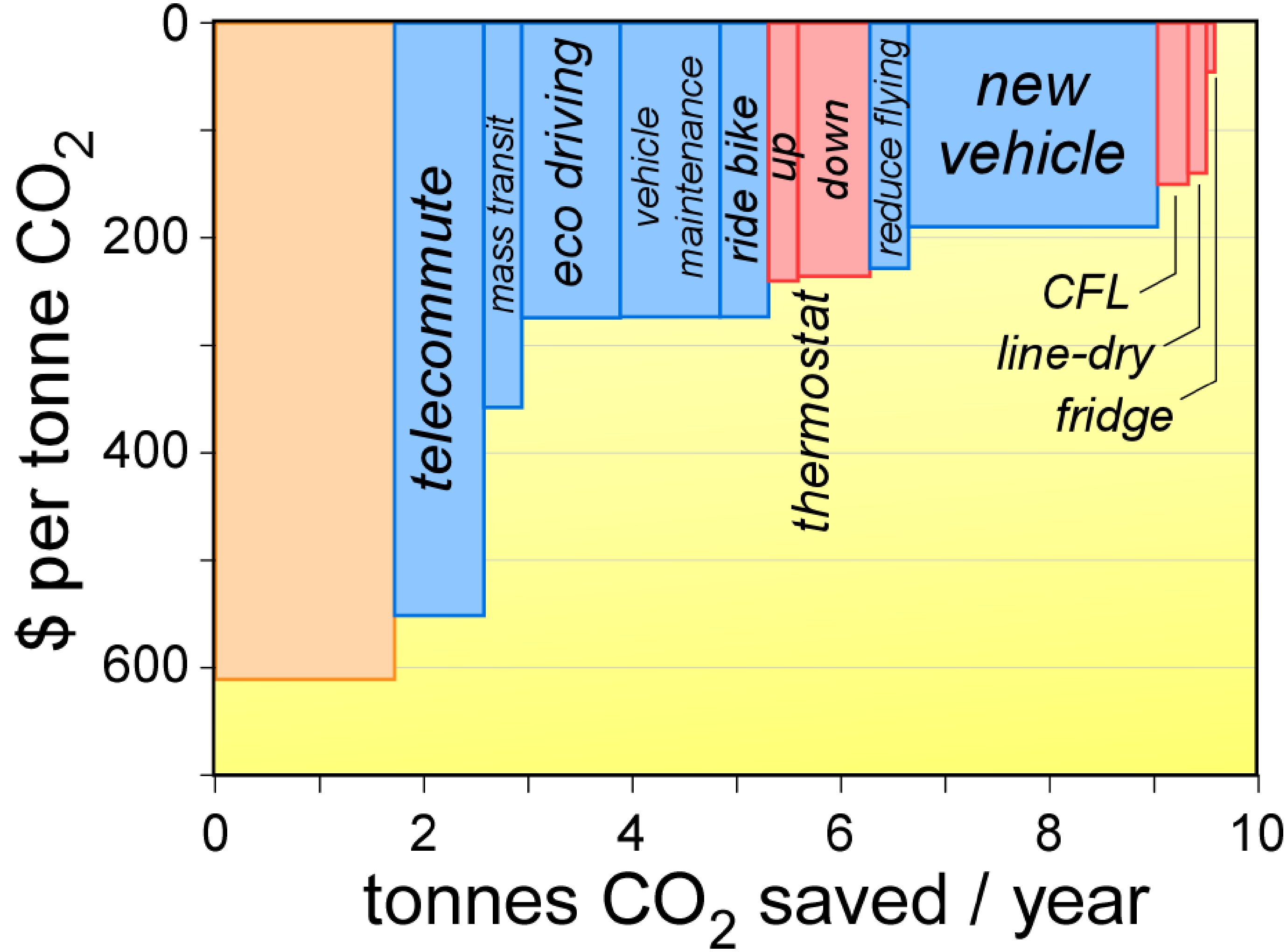
LumiGrow press release "Algae Farm Selects LumiGrow LED Horticultural Lighting
November 29, 2011

Algae Requirements

- water – and it must be fresh
- land – and it must be flat
- carbon dioxide – and atmospheric won't do
- sunlight
- nutrients



Average US Household Abatement Curve



Christopher M. Jones and Daniel M. Kammen; "Quantifying Carbon Footprint Reduction Opportunities for U.S. Households and Communities", *Environ. Sci. Technol.*, 2011, **45** (9), pp 4088-4095; DOI: 10.1021/es102221h

Summary

- switch from biofuels to biochemicals has issues
  - a failed fuels play doesn't automatically mean successful chemical economics
- practical algal biofuels have yet to be realized
  - water, land, CO2 and nutrients all are issues
- we can make anything from biomass if you're willing to pay
  - economics are not yet compelling and climate issues are not impacting the economics

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No Ag Bullet

Additional Info and Notes

Mark Jones

27 July 2011

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Abstract

The U.S. chemical industry a vital part of the U.S. economy. It is a $720 B enterprise making essential products that end up in 96% all manufactured goods. The industry uses both fossil and renewable resources to make products today. Bioproducts are receiving active interest due to consumer demand, industry interest in improved materials and interest from the biofuels community in making “high value chemicals”. Several inescapable principles must be dealt with in order to successfully navigate chemical production from biomass. These include:

– natural gas drives the chemical industry and halcyon days are expected due to shale gas
– biomass and biologically derived materials can be expensive raw materials for chemical production
– a mixture containing a valuable chemical is not the same as a valuable mixture of chemicals.

It is dangerous to assume that chemical production can save an economically challenged biofuels process. Repurposing a fuel for chemical use or garnering more value from co-products both are fraught with peril. Cautious optimism, rather than unbridled optimism, is in order as emphasis shifts towards bioproducts.

US Chemical Industry

- American Chemistry Council reports << http://www.americanchemistry.com/Jobs/EconomicStatistics/Industry-Profile/Industry-Facts/Chemistry-Industry-Facts.pdf>>
- 96% of all manufactured goods are enabled by chemistry
- Chemical industry has sales of over $720 billion
- Employs 800,000 people nationwide

US Chemical Industry

- Produce 19% of the world's chemicals - #1
- Exports of chemicals account for 10 cents of every dollar of total merchandise exports
- spend $49 B on R&D

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Dow Chemical

- over $53 B in sales
- diversified portfolio of specialty chemical, advanced materials, agrosciences and plastics businesses
- a global workforce of about 46,000 with approximately 21,000 in the US.
- Over 7000 R&D Employees
- >$1.6B Budget

Dow Chemical

- committed to U.S. manufacturing
- Dow CEO Andrew Liveris chairs the Obama Administration's Advanced Manufacturing Partnership << http://www.businesswire.com/news/home/20110624005345/en/Liveris-Named-Co-Chair-U.S.-President-Obama%E2%80%99s-Newly>>
- invested over $600 MM in past 5 years on USGC olefins supply chain
- announced billions more investment in restarts and new capacity in April

Biomass Program Goals

- A viable, sustainable domestic biomass industry that produces renewable biofuels, bioproducts and biopower, enhances U.S. energy security, reduces our dependence on oil, provides environmental benefits including reduced greenhouse gas emissions, and creates economic opportunities across the nation.
- from website, 20 July 2011

Ethanol barrels

- Thursday, July 14, 2011
- **CME: Ethanol Averaged 872,000 Barrels/Day**
- **550,000 Barrels Oil Eq / Day**
- US - Ethanol production for the week ending July 8 averaged 872 thousand barrels per day. This is down 32 thousand barrels per day (-3.54 per cent) vs last week and up 51 thousand barrels per day (6.21 per cent) vs last year.
- Total ethanol production for the week was 6.104 million barrels, down 224 thousand barrels vs last week and up 357 thousand barrels vs last year. Corn used in last week's production is estimated at 91.56 million bushels.

  This crop year's cumulative corn used for ethanol production for this crop year is 4.15 billion bushels.

  Corn use needs to average 116.16 million bushels per week to meet this crop year's USDA estimate of 5.05 billion bushels.

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EISA

- the 2007 Energy Independence and Security Act.
- It requires the use of three alternative fuels: car and truck fuel made from cellulose, diesel fuel made from biomass and fuel made from biological materials but with a 50 percent reduction in greenhouse gases.
- The goal set by the law for vehicle fuel from cellulose was 250 million gallons for 2011 and 500 million gallons for 2012.
- less than 6 is available

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Chemical Supply

- Science 31 July 1981:
- Biomass as a Source of Chemical Feedstocks: An Economic Evaluation
- B. O. Palsson, S. Fathi-Afshar, D. F. Rudd and E. N. Lightfoot

- It is suggested that the raw materials and technology exist for basing a major fraction of the U.S. chemical industry on four fermentation products, used in the proper portions: ethanol, isopropanol, n-butanol, and 2,3-butanediol. The primary route for introduction of these materials is dehydration of the alcohols and diols to olefins, which would cause little disruption of the existing industry downstream from the olefins. The proposed substitution has the advantages that it would provide a smooth transition toward renewable feedstocks, while decreasing dependence on fossil sources of organic material and use of toxic materials. However, to make these materials attractive as feedstocks or intermediates in chemical production, their current prices must be substantially reduced. Even with the optimum mix, their large-scale utilization will only occur at about 20 to 40 percent of their estimated chemical prices.

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Product Recovery

- separations are expensive!

  "Exact figures may be hard to come by, given the complexity of the chemical industry, but separation processes have been estimated as accounting for somewhere between 40% and 70% of its capital and operating costs."

  Spear, Mike; "Stretching separation choices", Chemical Processing, February 2006, pages 18-22.

- separations, especially distillations, scale very well
  - biomass to still, not still to biomass

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