GEOS 24705 / ENST 24705
Fossil fuels III

Fossil fuels – buy organic matter and expose to high T, P

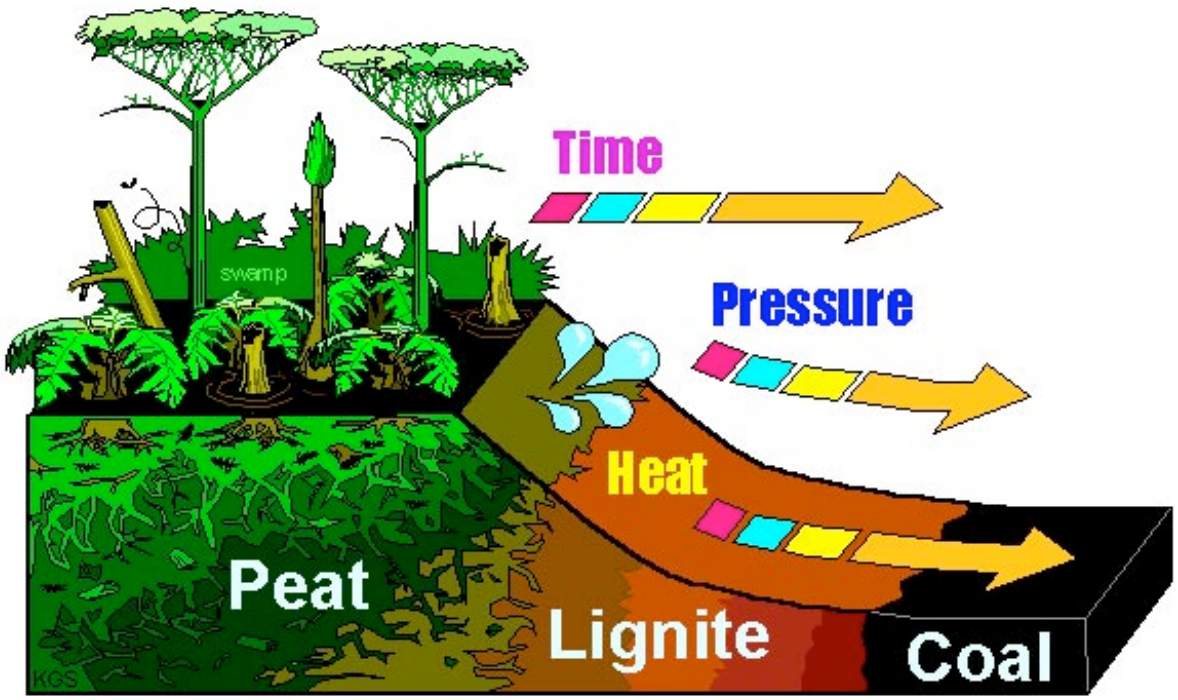


Image: Kentucky Div. of Mine Permits

Requires anaerobic conditions to prevent oxidation

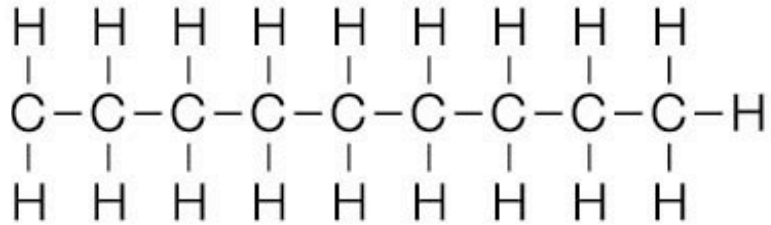
Heat and pressure cause gradual changes composition: drive off water, react off O, new compounds form

Energy density increases during process from ~ 20 MJ/kg to up to > 40 MJ/kg

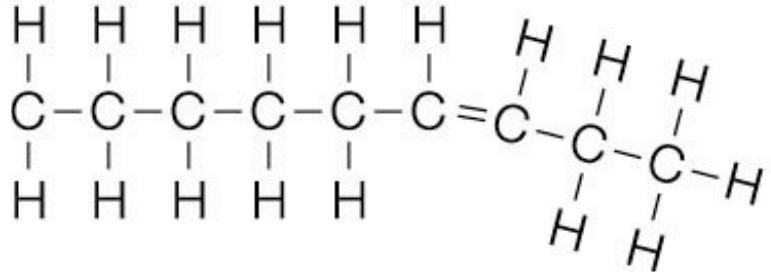
Molecular composition of fats and hydrocarbons

Fats are similar in energy density to oil, but aren't hydrocarbons.
Remove COOH units however and become hydrocarbons

Saturated



Unsaturated



"Saturated" means no double C bonds – no extra place where a new atom could be incorporated in chain. (Each C "wants" to have four bonds).

As fossil fuels are geologically processed:

both composition and energy density change

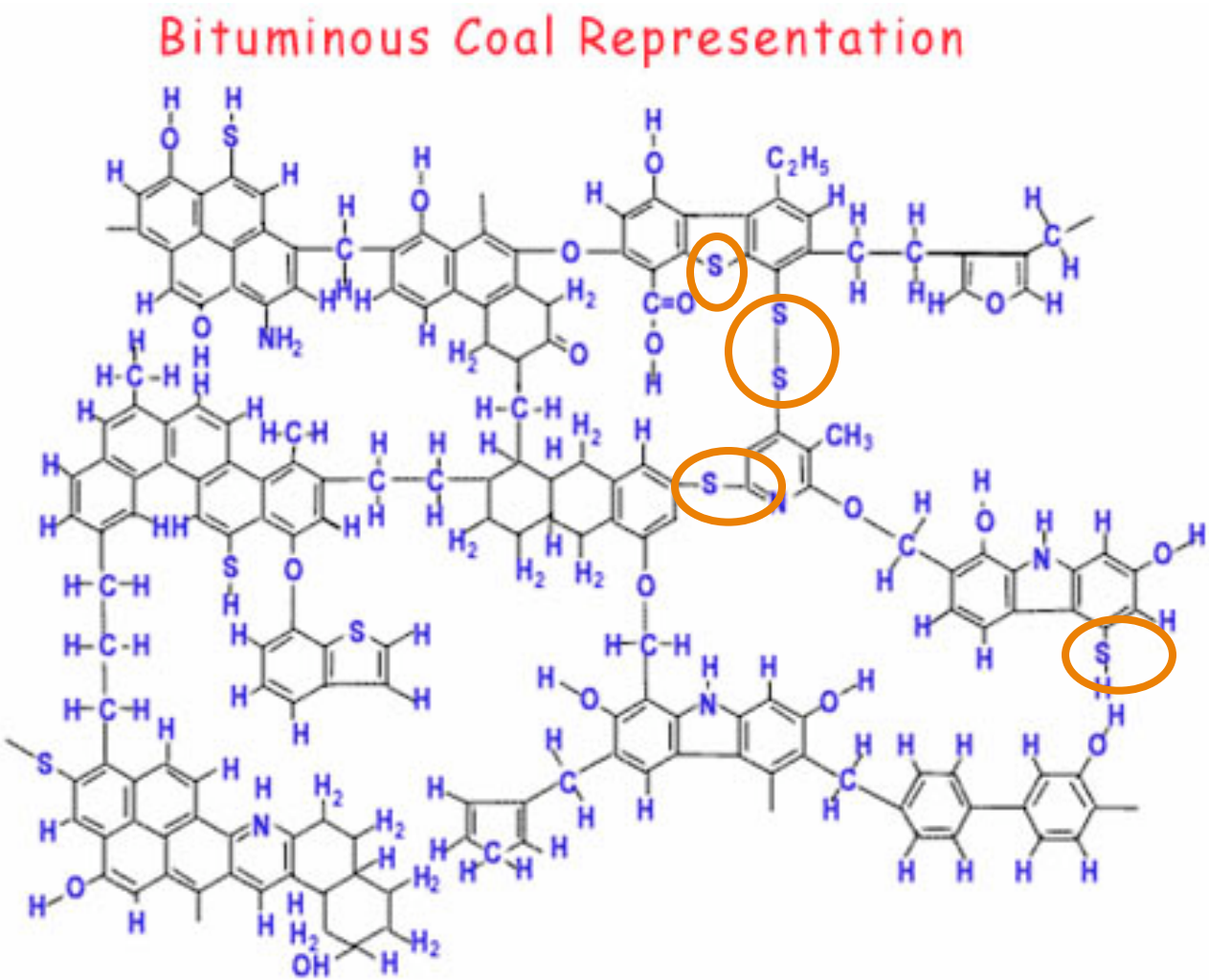
	C:H:O	Energy density (MJ/kg)
Dry biomass (or peat)	1 : 1 : 0.4	10-30
Coal	1 : 0.8 : 0.1	20-35
Crude oil	1 : 1 : 0.02	~42
Refined petroleum	1 : 2 : 0	44-47
Natural gas	1 : 4 : 0	50

Oxygen loss: Processing of fossil fuels in Earth drives off oxygen, lowers total energy content … but increases energy density in stuff that remains. (Also drives off water).

Carbon/hydrogen separation: volatiles with lower C:H can separate out (natural gas, petroleum distillation).

Molecular composition of coal

mineral structure, complex and highly variable (mostly C & H)

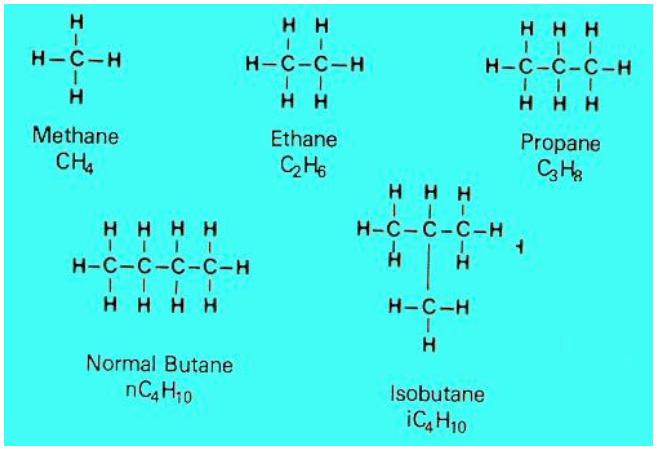


Not all C, H, and O – some sulfur impurities. If burnt in a combustion chamber without a sulfur scrubber, S oxidizes to become sulfur dioxide, or SO_2, which then makes sulfuric acid (H_2SO_4) and acid rain.

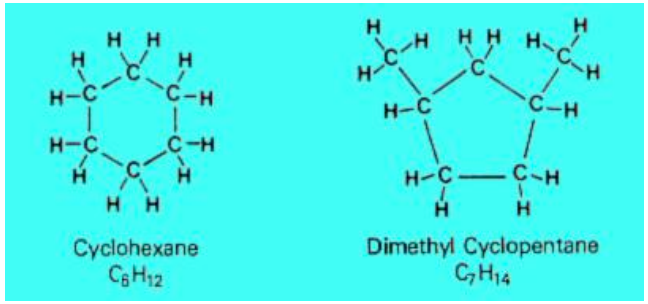
Theoretical model of "typical" coal, from Western Oregon University

Molecular composition of crude oil

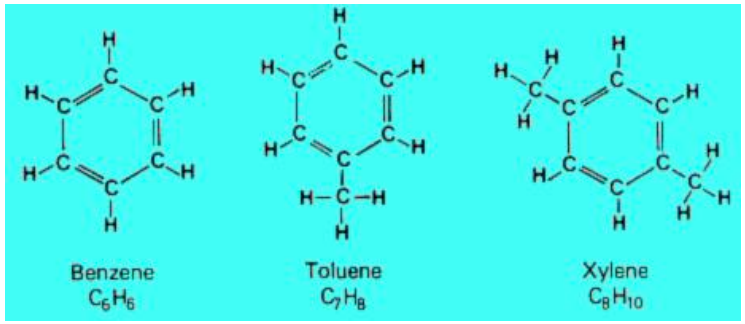
Also complex – a mixture of hydrocarbons C_nH_m of various lengths to > C_{70} (with some impurities, e.g. sulfur at S:C ~ .004-.02: 1)



Paraffins



Naphthenes



Aromatics

Crude oil includes both saturated and unsaturated compounds.

Long-chain hydrocarbons make crude viscous

Canadian crude has viscosity similar to molasses, can get 10 x more viscous

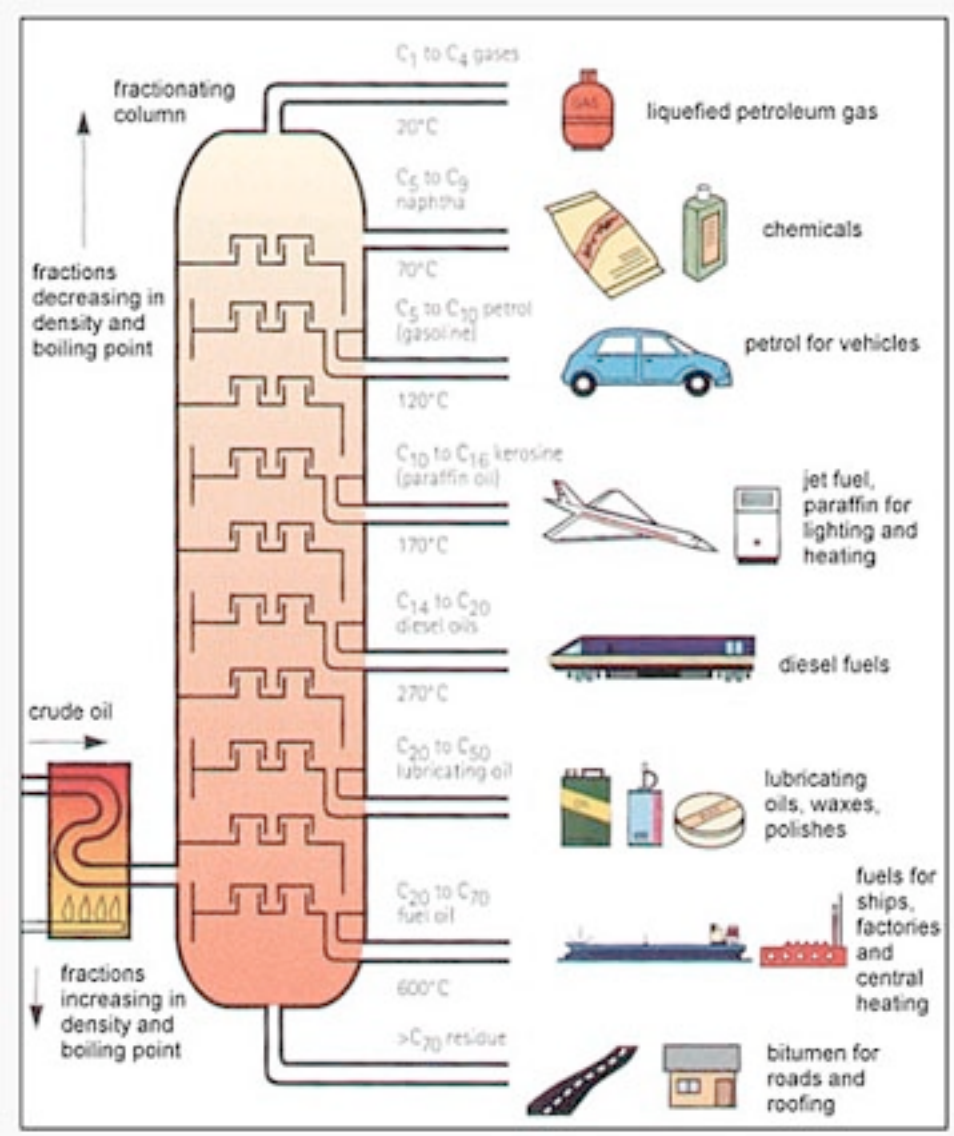
Soldiers from the South Korean army clean up crude-oil spills over Mallipo Beach after an accident involving a Hong Kong-registered tanker in Taean, about 106 miles southwest of Seoul, on December 10, 2007.

Petroleum refining = separating crude oil into components, also altering chemistry of those components

1 Distillation – separating components of crude oil

2 Catalytic cracking – breaking down components

3 Reforming – combining constituents



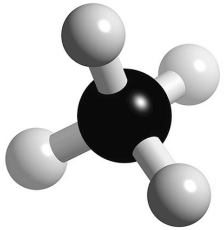
Distillation column. *Image: theOilDrum.com*

Burning hydrocarbons

Energy extracted by breaking and reforming bonds

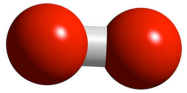
e.g. oxidizing (burning) natural gas:

$$CH_4 + 2 \bullet O_2 \rightarrow CO_2 + 2 \bullet H_2O$$



4 C-H bonds

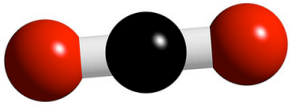
and 2 O=O bonds

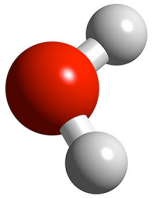


X 2

2 C=O bonds

and 4 O-H bonds



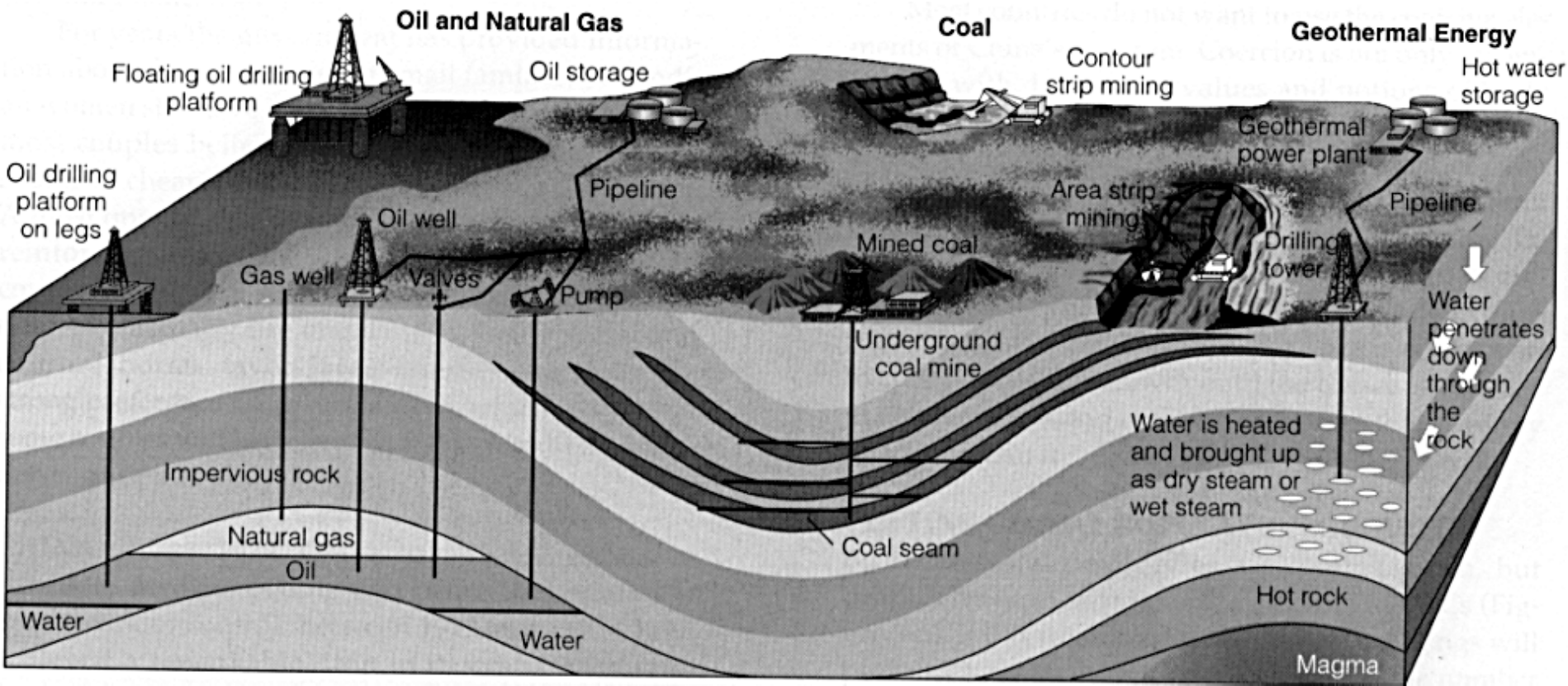


X 2

3 D images from 3Dchem.com

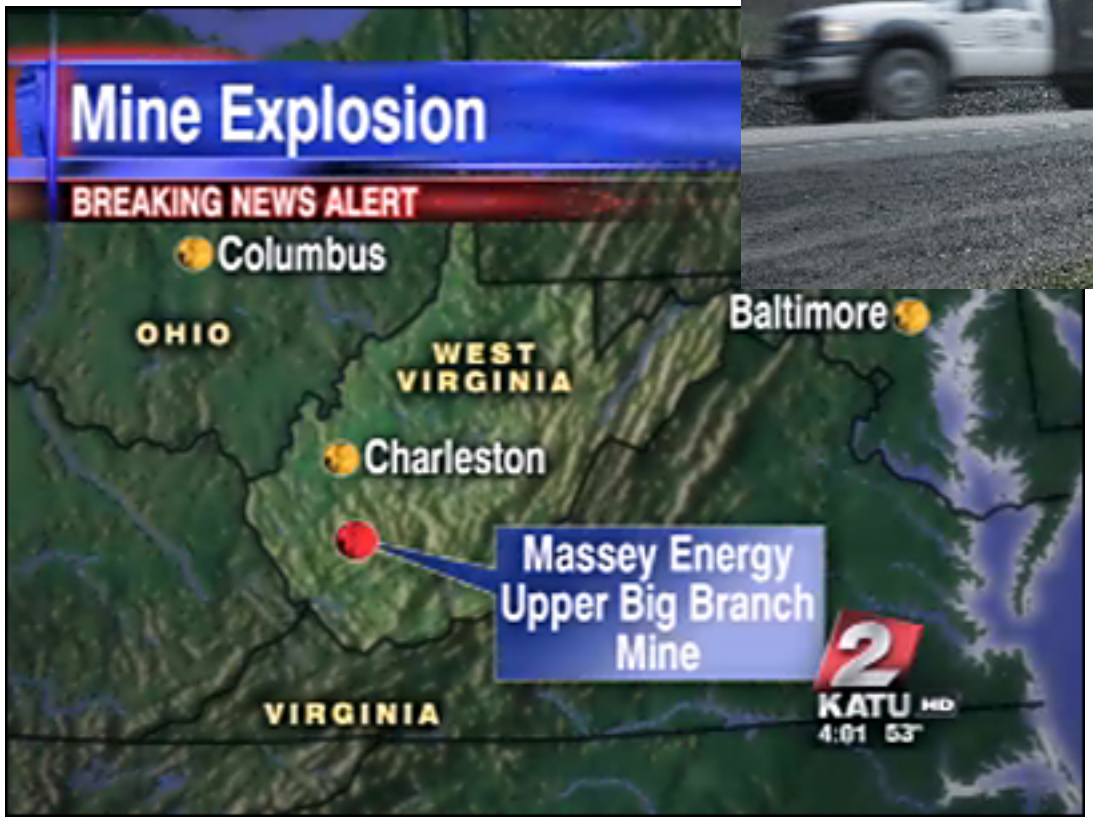
Where are fossil fuels found?

- *Oil and gas:* migrate from source beds, lighter than water, trapped in anticlines under impervious sediments (shale, clay)
- *Coal:* remains in place, found when beds (or "seams") are brought near surface (typ. mine depths surface to 300 m). Seams thin, typ. 3-10 ft thick



Much gas is associated with oil, but some is found with coal:
why coal mining is so dangerous

Thousands of deaths each year in Chinese coal pits; 30 a year in the U.S.



News flash and local signs after 2010 explosion at Massey W. Virginia mine

R: Mark Humphrey, Associated Press

A digression on coal seam methane

(or, the history of energy technology is a very small world)

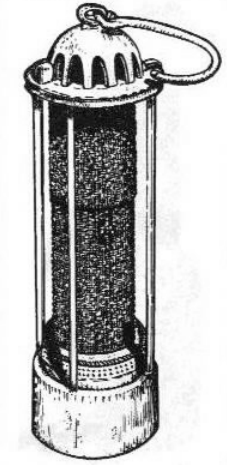
As coal mines got deeper in Britain, miners were dying from methane explosions ignited by their lamp flames. 1812 Felling explosion prompted simultaneous invention of safety lamps by

the chemist Humphry Davy

Sicherheitslampe

who bitterly accused each other of IP theft

and the engineer George Stephenson

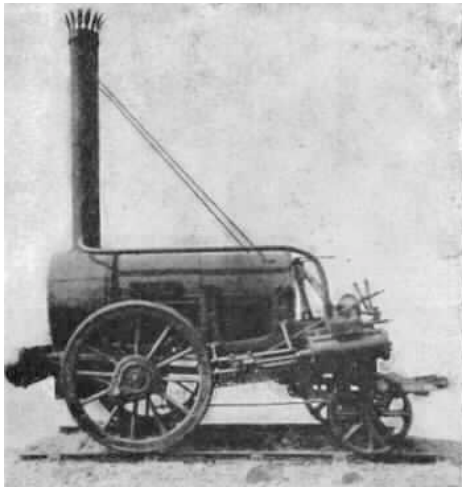


Stephenson's "GEORDIE" lamp.

Davy employed Michael Faraday

who gave us Faraday's law and the electric motor…

…while Stephenson turned to locomotives and invented the 1829 Rocket



No labor laws in 1812

15 of 92 miners killed in Felling were 12 and under – youngest was 8

Where is coal found?

Coal: biggest reserves U.S., Russia, Canada, Australia, China

Coal gradations

peat

lignite

sub-bituminous

bituminous

anthracite

Age / processing

Where is coal found?

U.S. has world's largest coal reserves. Anthracite coal peaked in 1920s but lower grades have larger energy content than total world oil reserves.

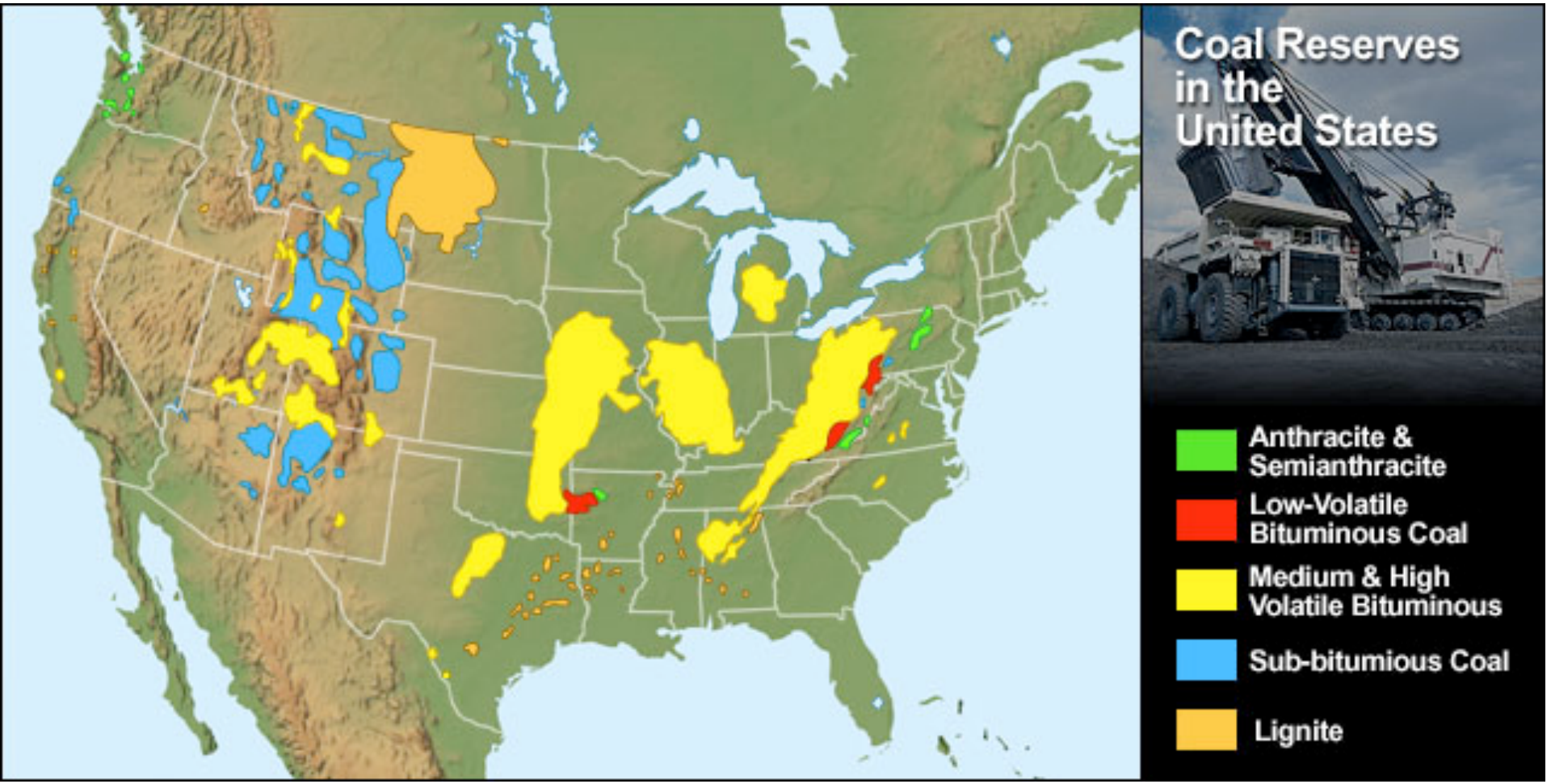


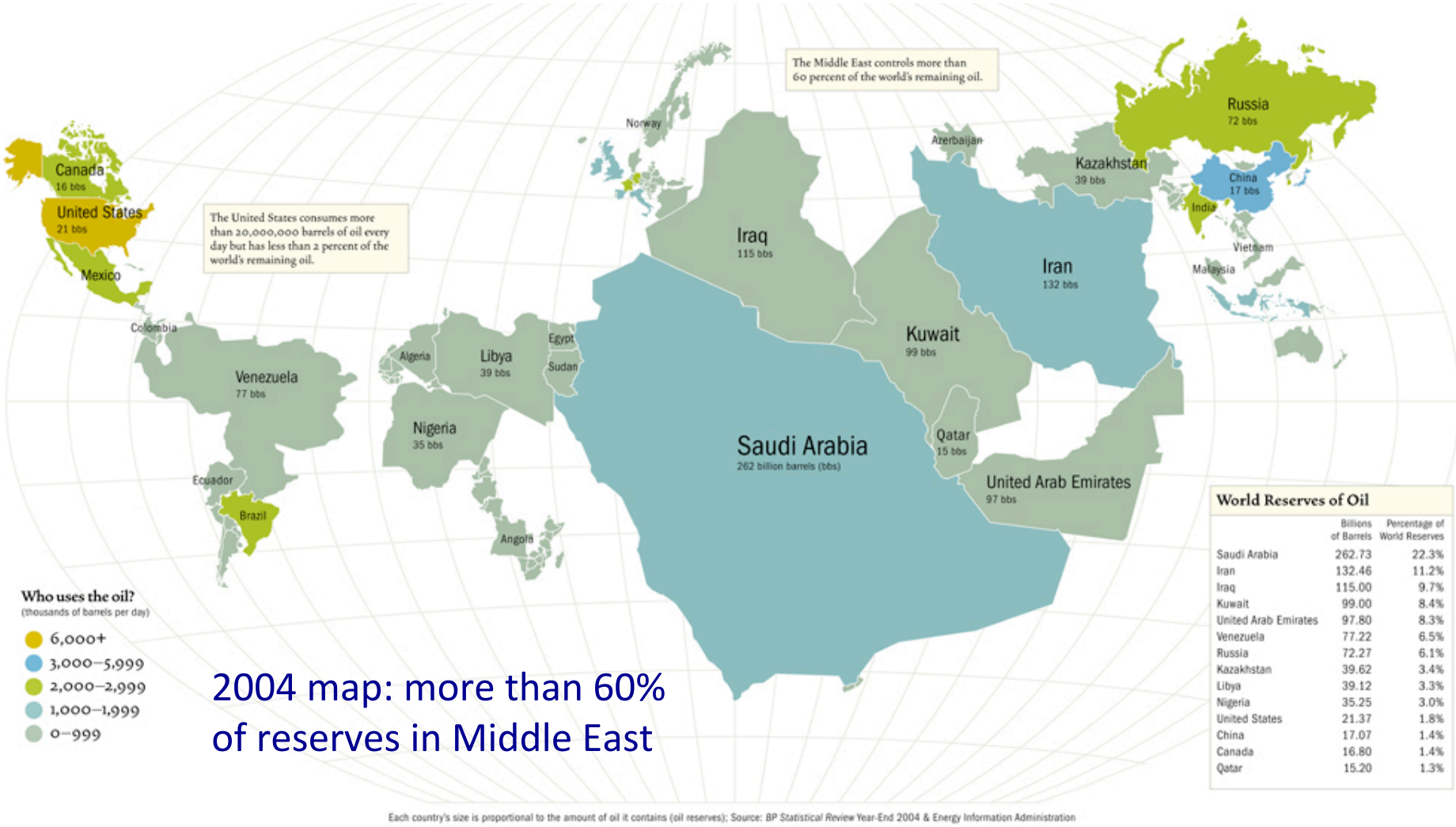
Image: American Coal Foundation

Data: Speight, J.G. "The Chemistry and Technology of Coal"

Biggest production: Wyoming, Kentucky, W. Virginia, Pennsylvania, Illinois (but PA and IL peaked in 1918, PA coal down by factor of 4 since)

Sulfur content: Western coal < 0.5%. Midwest coal > 1.5%

Where is oil found?

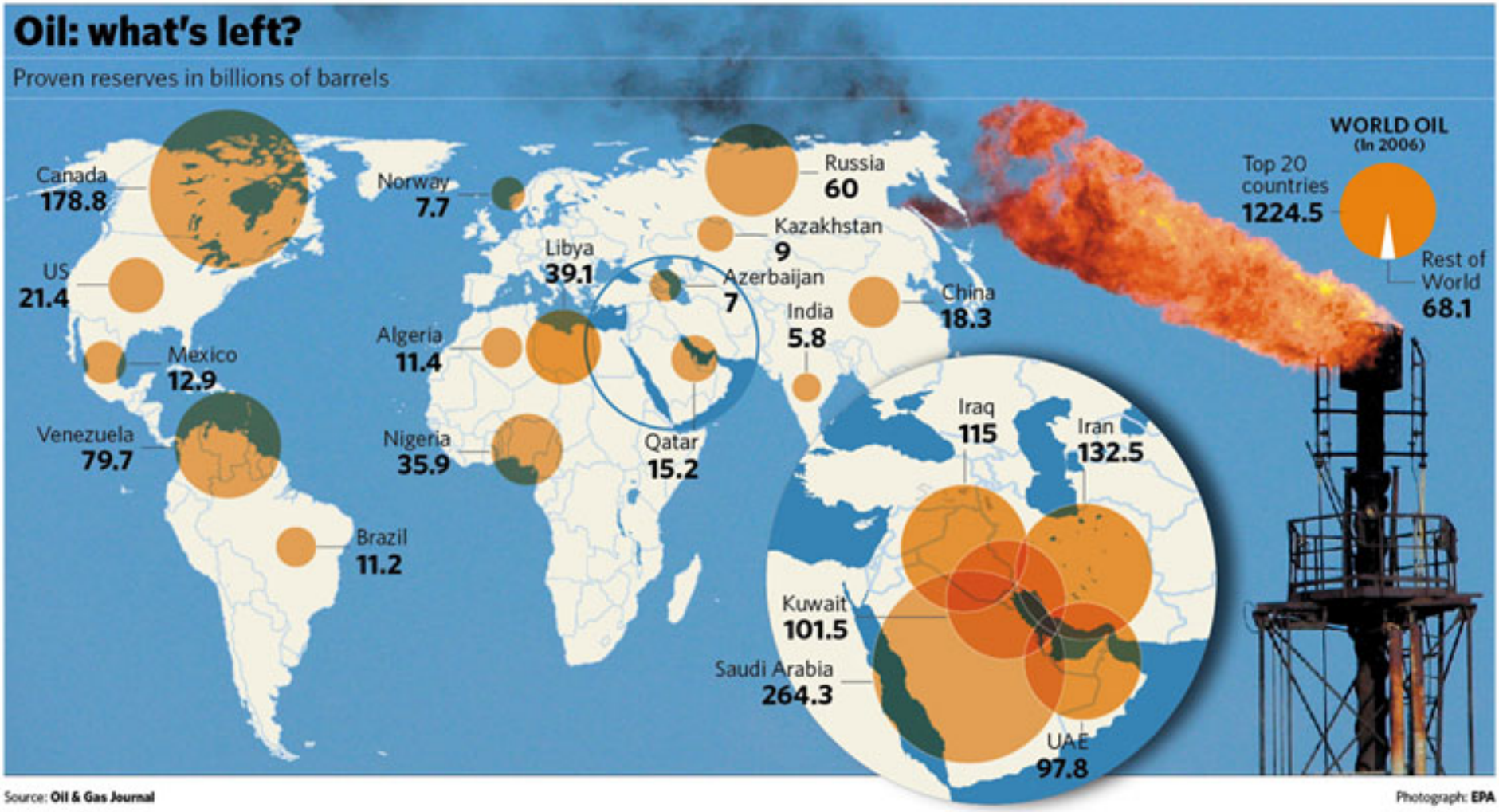


World Reserves of Oil

	Billions of Barrels	Percentage of World Reserves
Saudi Arabia	262.73	22.3%
Iran	132.46	11.2%
Iraq	115.00	9.7%
Kuwait	99.00	8.4%
United Arab Emirates	97.80	8.3%
Venezuela	77.22	6.5%
Russia	72.27	6.1%
Kazakhstan	39.62	3.4%
Libya	39.12	3.3%
Nigeria	35.25	3.0%
United States	21.37	1.8%
China	17.07	1.4%
Canada	16.80	1.4%
Qatar	15.20	1.3%

Map: Energy Bulletin. Data sources: BP Statistical Review Year-End 2004 and the Energy Information Administration.

Where is oil found?

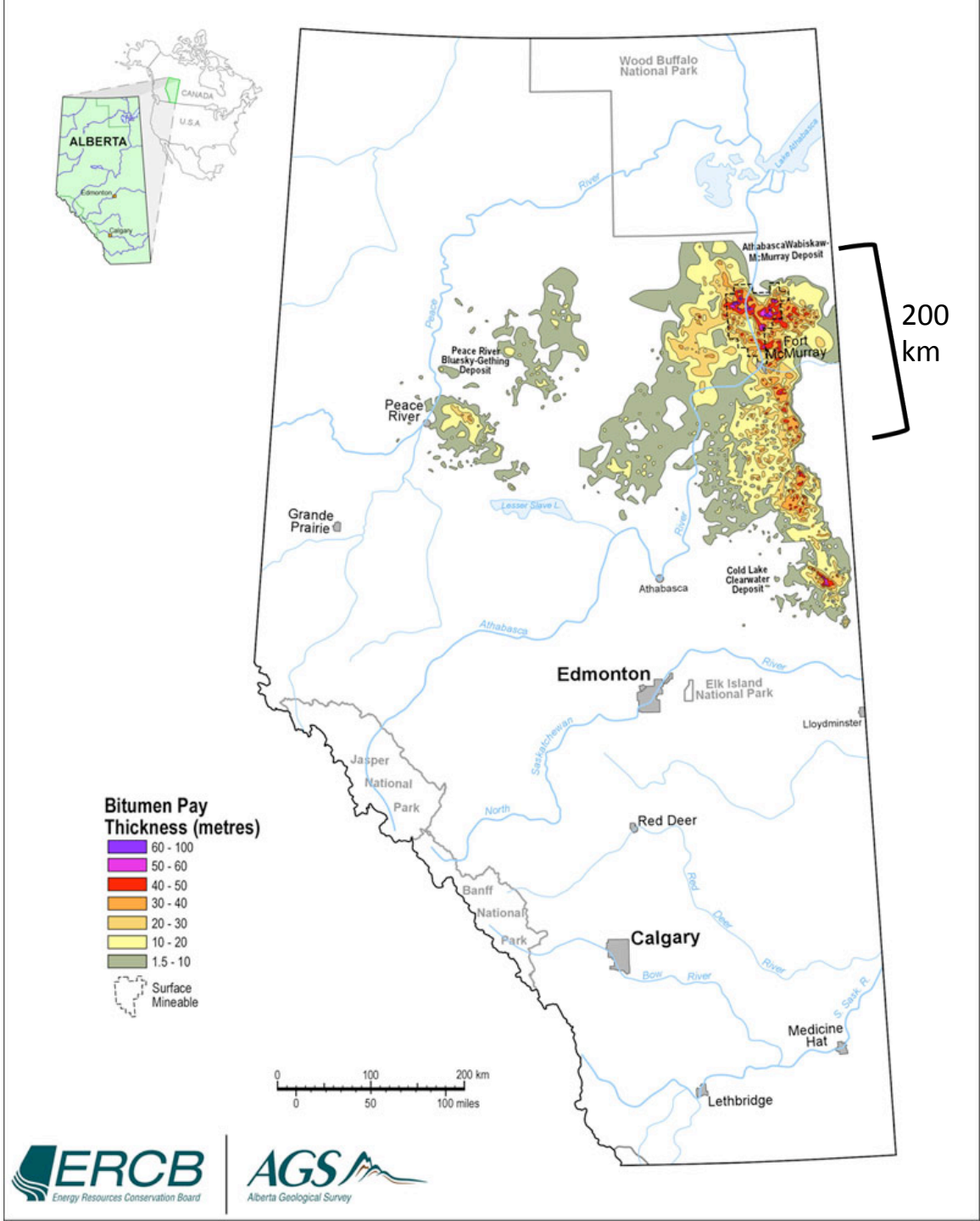


Alberta oil sands

Localized deposit (but 140,000 km^2)

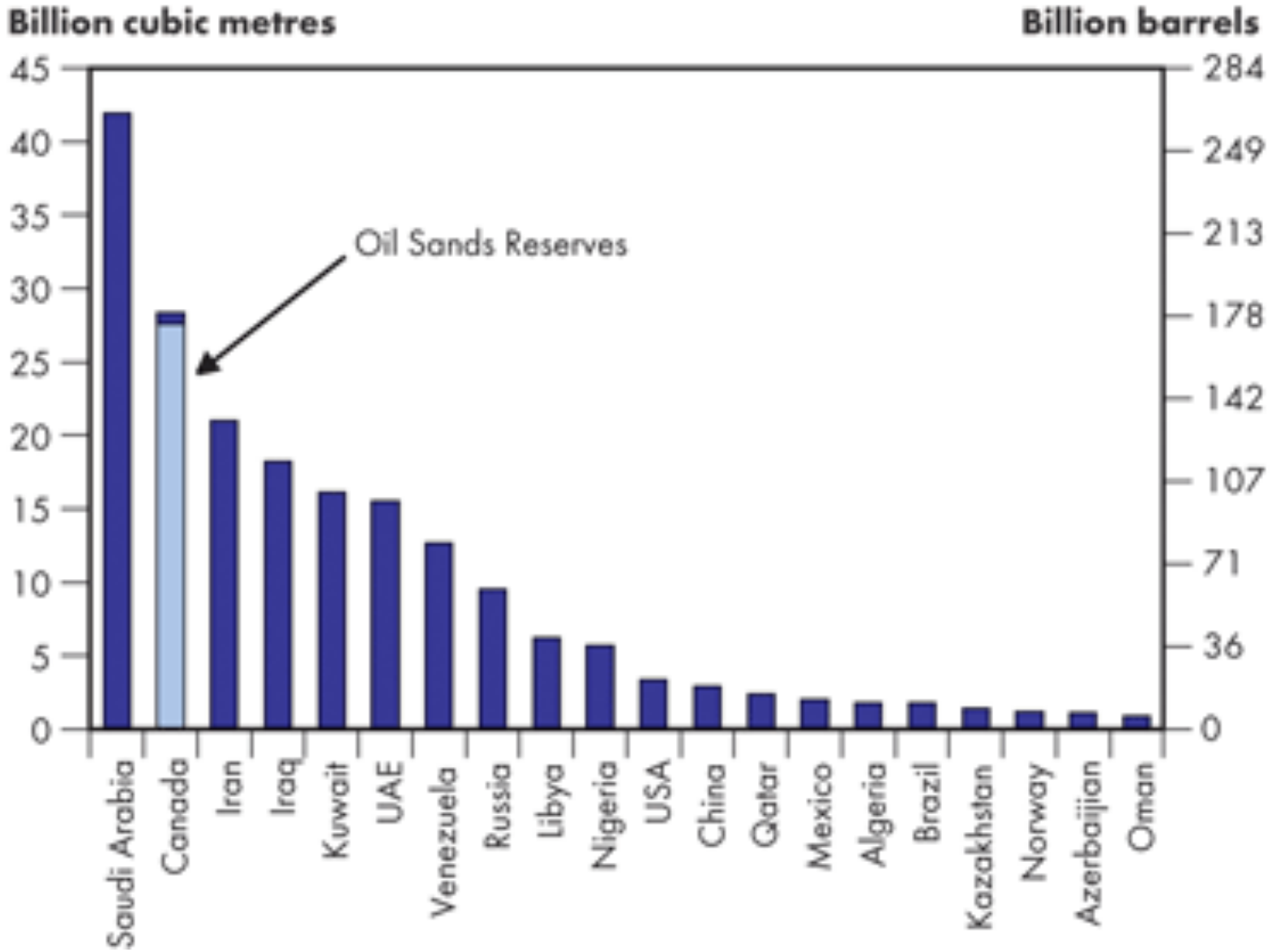
Production: 1.3 M barrels/day in 2008, to increase to 3M bbl/day

Investment: $14B in 2006



From: Alberta Geological Survey

Oil sands are significant addition to world oil reserves



History of oil production

Modern era begins with first well in Titusville, 1859

Site is long known "Oil Creek", oil was nuisance. Purposeful drilling for oil instigated by businessmen looking for lighting alternative

Oil production boomed by x 1500 in 4 yrs, x 5000 in 15 years

Phillips and Woodford wells on Oil Creek, PA, 1861

From Pennsylvania Historical & Museum Commission, Drake Well Museum Collection, Titusville, PA

Oil production then takes off

Refineries and pipelines by 1870s (Rockefeller's Standard Oil founded 1870) *– for kerosene, gasoline was waste product – too volatile and flammable for use for lighting*

1878: Edison's lightbulb reduces kerosene demand, causes oil industry slump

1886: invention of car provides market for gasoline

By WWI U.S. is dominant oil producer (TX, CA) and exporter, followed by Russia

Oil barrels (1860s?) Titusville.

As much as 50% of oil was lost to spillage in production & transport *(Paleontological Research Assn.)*

Middle east modern oil industry has roots just as long

First drilled oil well in Baku, Azerbaijan in 1848 (before Titusville)

Nobel oil field in Balakhani, Azerbaijan, 1890s – Swedish-owned by Nobel brothers, one of whom goes on to invent dynamite and found a famous prize…From: San Joaquin Geological Society

High-pressure oil, no need for pumps – derricks only

R: Baku, Azerbaijan, 1890, building levees to try to save oil from gusher. *Image from: San Joaquin Geological Society*

L: The famous 1901 Lucas gusher in Spindletop dome, Texas, gushing more oil than the rest of the country's production together. *Image from: American Petroleum Institute*

No more gushers: lower-pressure oil requires a pump

"Nodding donkeys": beam pump to pump liquids from ground

Image: Tony Waltham

Not a true beam engine. Typically use diesel engines, but reciprocating cylinders -> rotary motion and then -> linear motion of larger beam.

Can't use linear motion of diesel engine cylinders since are too short and move too quickly.

Gearbox
http://www.youtube.com/watch?v=FU0dYV3LvAk&feature=related

Sucker rod pump:
http://www.youtube.com/watch?v=SFJFiyXTOa0

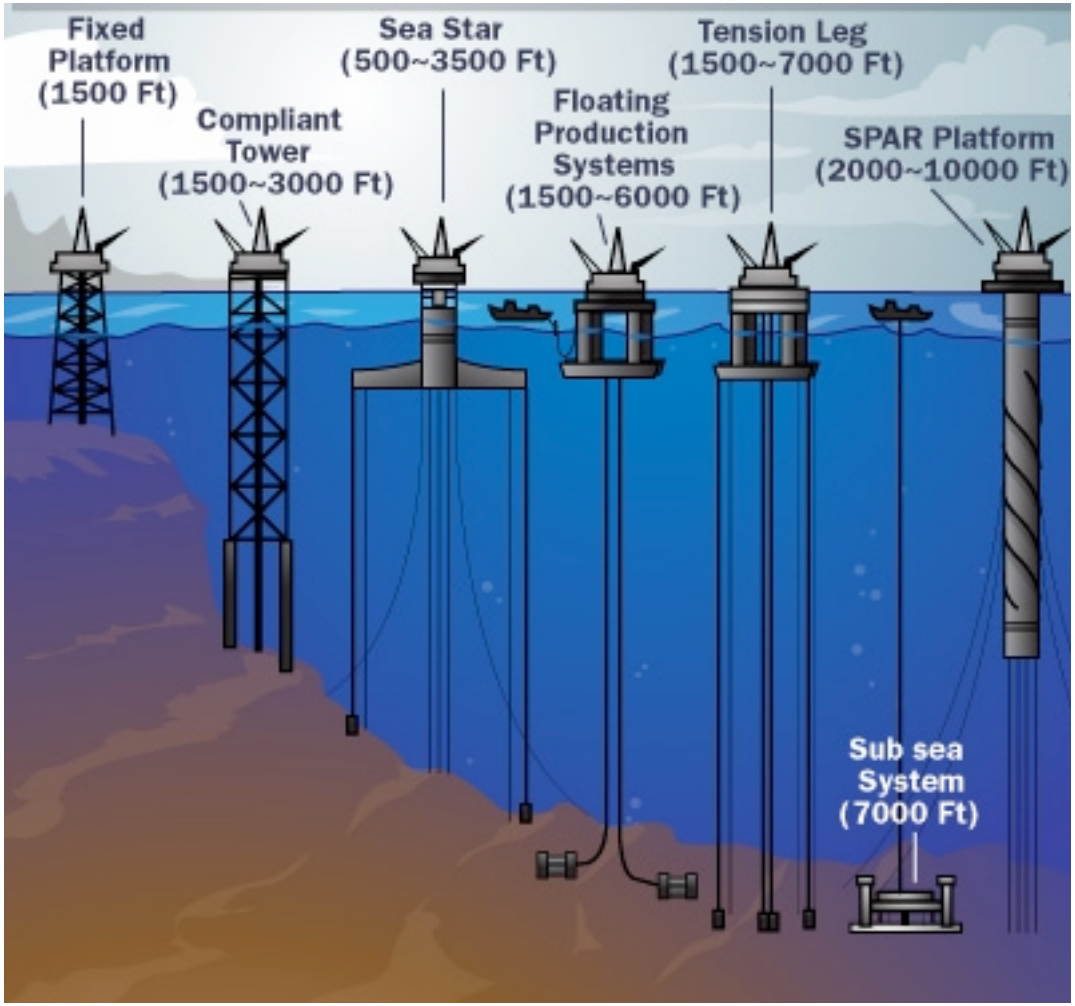
Exhaustion of "easy" U.S. oil means increasing complexity of extraction and transport distance

First offshore platform off Louisiana in 1938 (100 foot depth)
After WWII oil in Arabian Middle East developed
1973 OPEC embargo prompted construction of Trans-Alaska pipeline (1977)
Now
Enhanced oil recovery (gas or CO_2 injection, steam heat) squeezes oil from marginal fields
Major production from oil sands began ~ 2003
Oil produced from deeper and deeper waters: BP "Deepwater Horizon" is 5000 ft (1500 m)
Industry projected extraction from 8000 ft water depths … and wells to > 35,000 ft.

Petrobras P-51 oil and gas platform off the Brazilian coast: 180,000 barrels oil and 6M cubic meters gas per day.

Photo: Petrobras

Floating oil platforms allow deepwater production



Wells drilled from drill rigs, then replaced by production platforms. One platform can serve many slant wells, processing to separate oil from mud, gas, water, etc.

Generally wells need pumping. No rod pumps though! Too deep for them.

Blowout prevention system (BOP) seals well if back pressure detected.

Figure above: HowStuffWorks.com

Left: Solar Navigator.net

Hibernia platform, world's largest oil platform, N. Atlantic off Canada, gravity base structure, 50 wells drilled

Oil or tar sands = liquid crude embedded in solid matrix

Extract by:

- Digging sands up for processing
- Underground heating by steam injection to make heavy oil (bitumen) less viscous and able to be pumped
- Underground heating by burning some of the oil sands and again pumping

Two tons of tar sand make 1 barrel of oil –

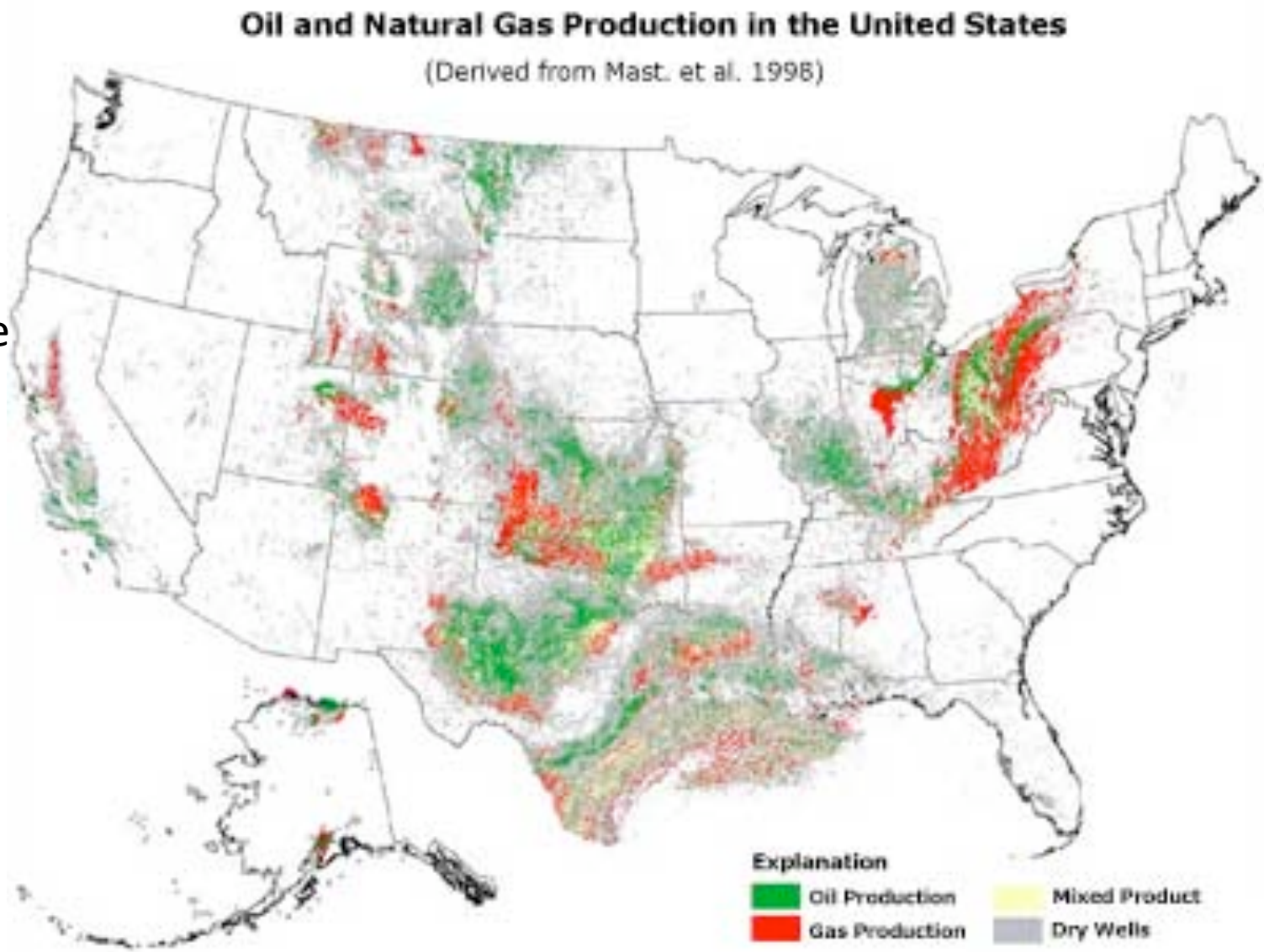
Oil only 1/10th the mass

Alberta tar sands, Canada. *Photo source: Suncor Energy Inc.*

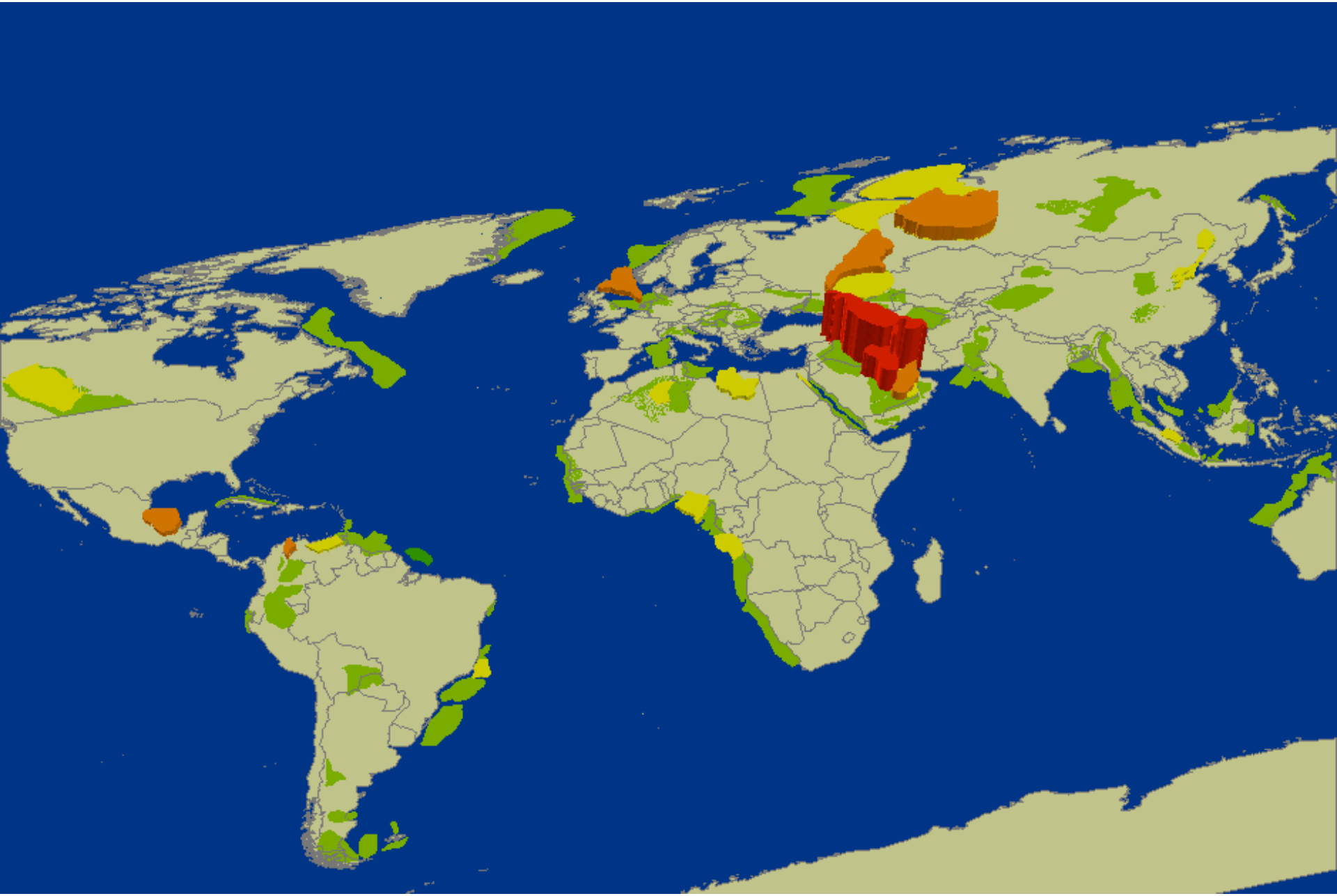
Oil and gas tend to be found in proximity

Gas tends to go along with oil, since formed by same process, trapped by same geological features.

Also goes along with coal – source of methane explosions in mines



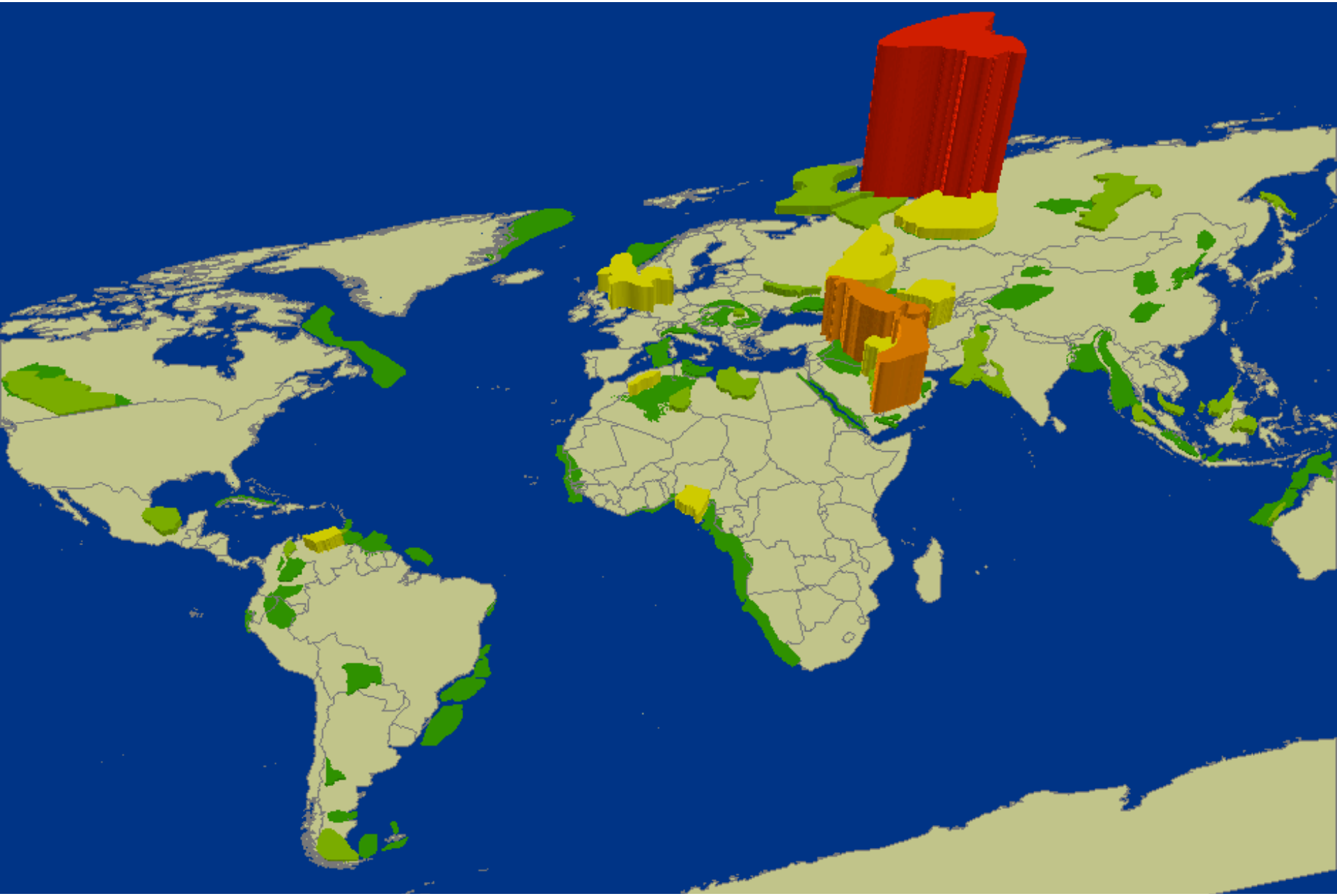
World proven oil reserves



Notice that U.S. doesn't even register on global map.

Source: FortiusOne Data: USGS World Petroleum Assessment

World proven conventional gas reserves

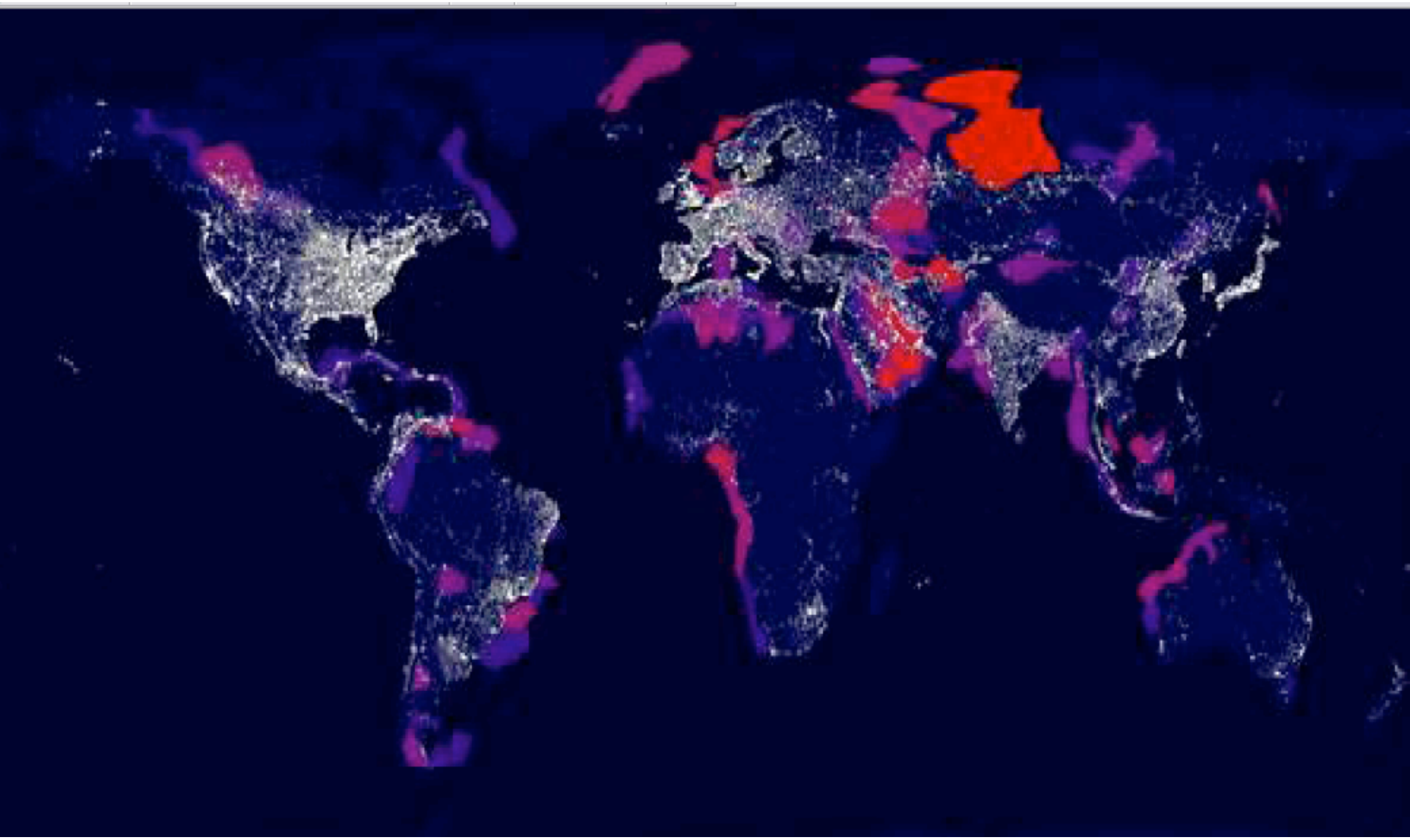


Notice that U.S. doesn't even register on global map.

Source: FortiusOne Data: USGS World Petroleum Assessment

Demand and production are in different places

Oil + gas are purple and red, electric lights are rough proxy for demand



From: Hartley, Medlock, and Nesbitt. "Russian Natural Gas Supply: Some Implications for Japan" (presentation). Baker Inst., Rice Univ.

Mismatch between production and demand -> transport

How are fossil fuels transported?

Coal

Railroads overland

Typically little international sea transport, except…

…shipping from Australia to China

Oil

Pipelines -> ships (oil tankers) and sea transport

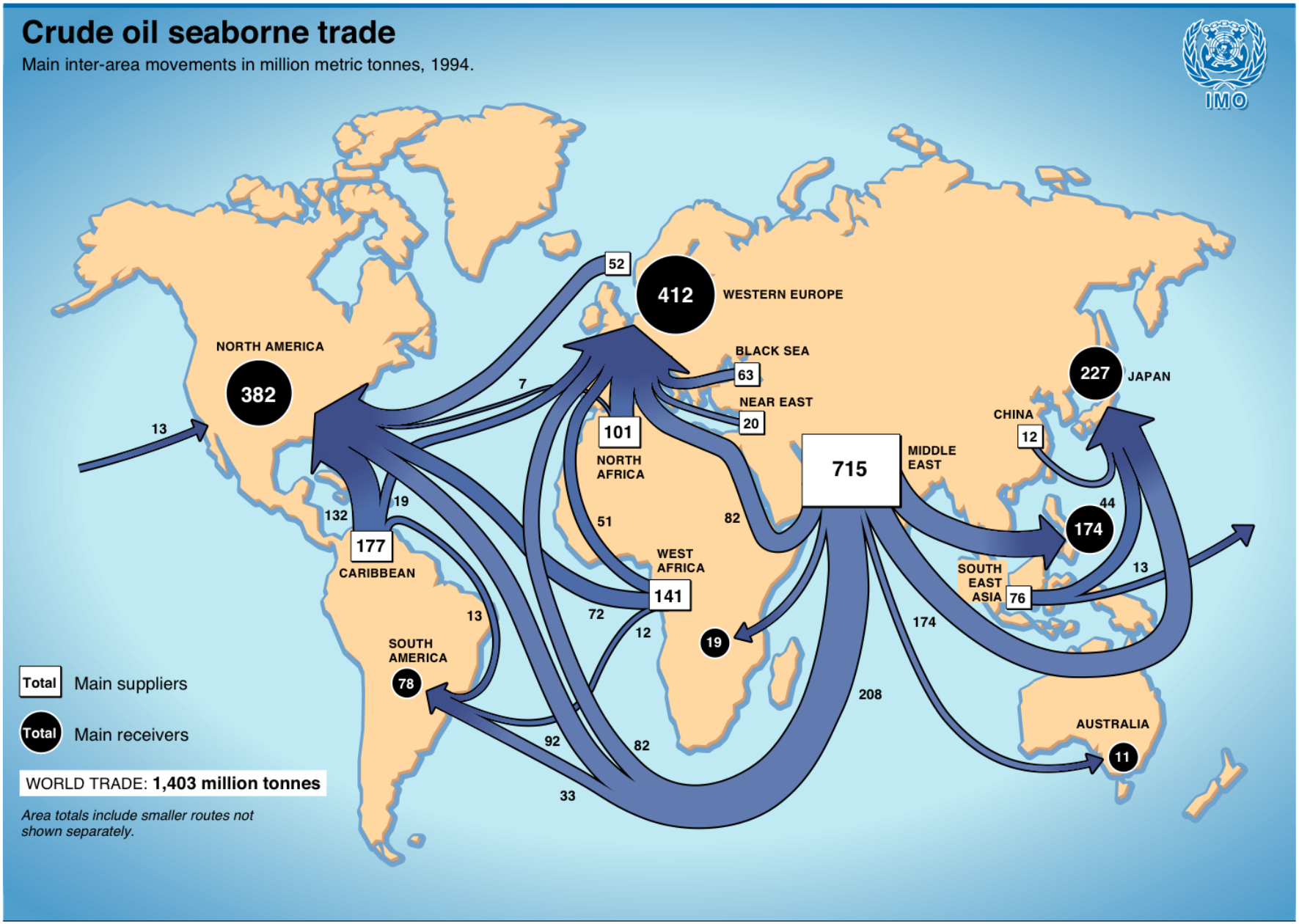
Gas

Pipelines (gas phase) overland only

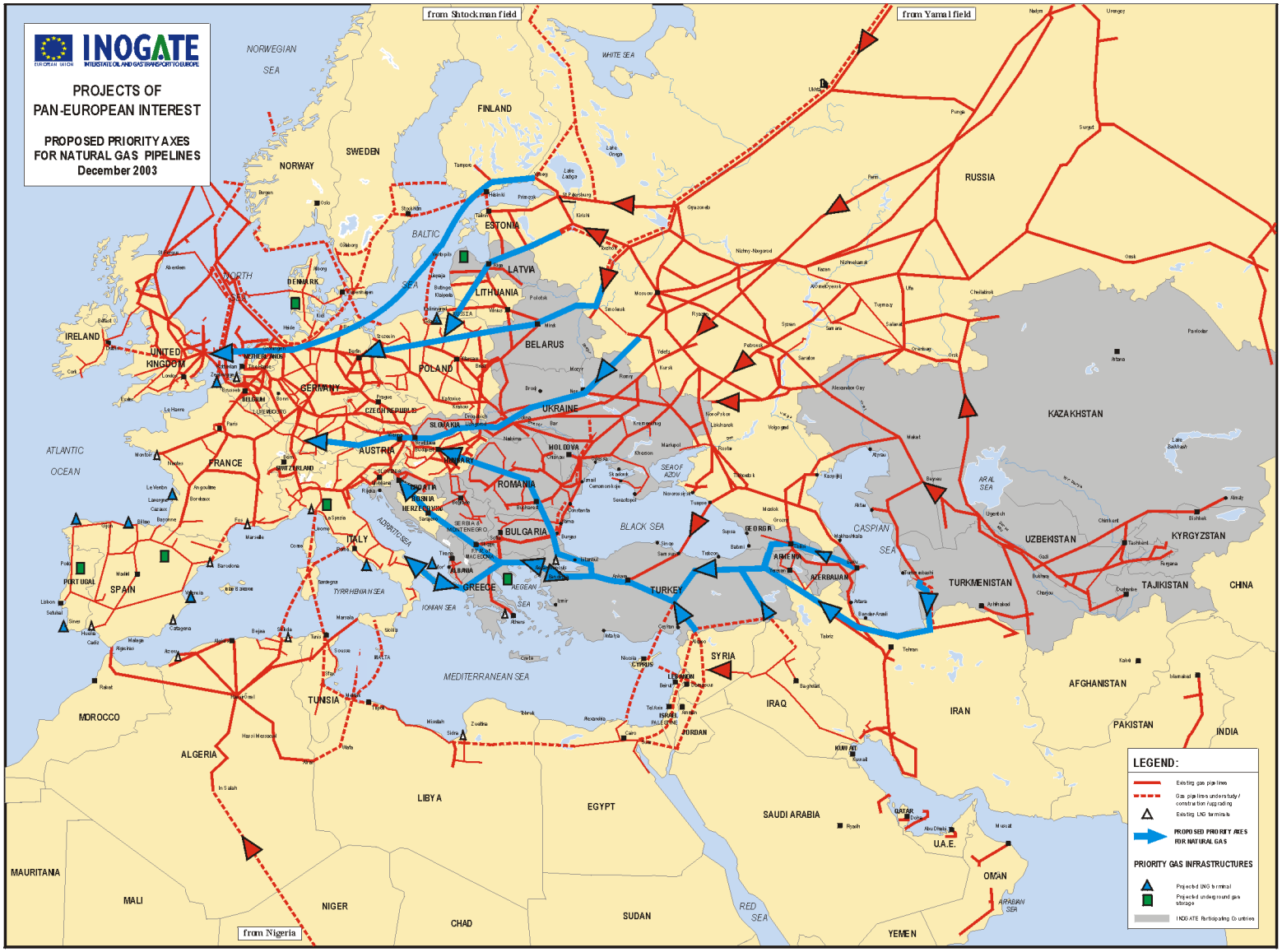
Can be moved by ship if compressed until it liquifies. ("LNG" = liquified natural gas) But NIMBY issues with LNG: highly explosive, dangerous, no one wants an LNG terminal near them

Consequence: oil prices are global, coal and gas are local

Oil largely moved by sea in tankers



Gas is mostly moved overland in pipelines



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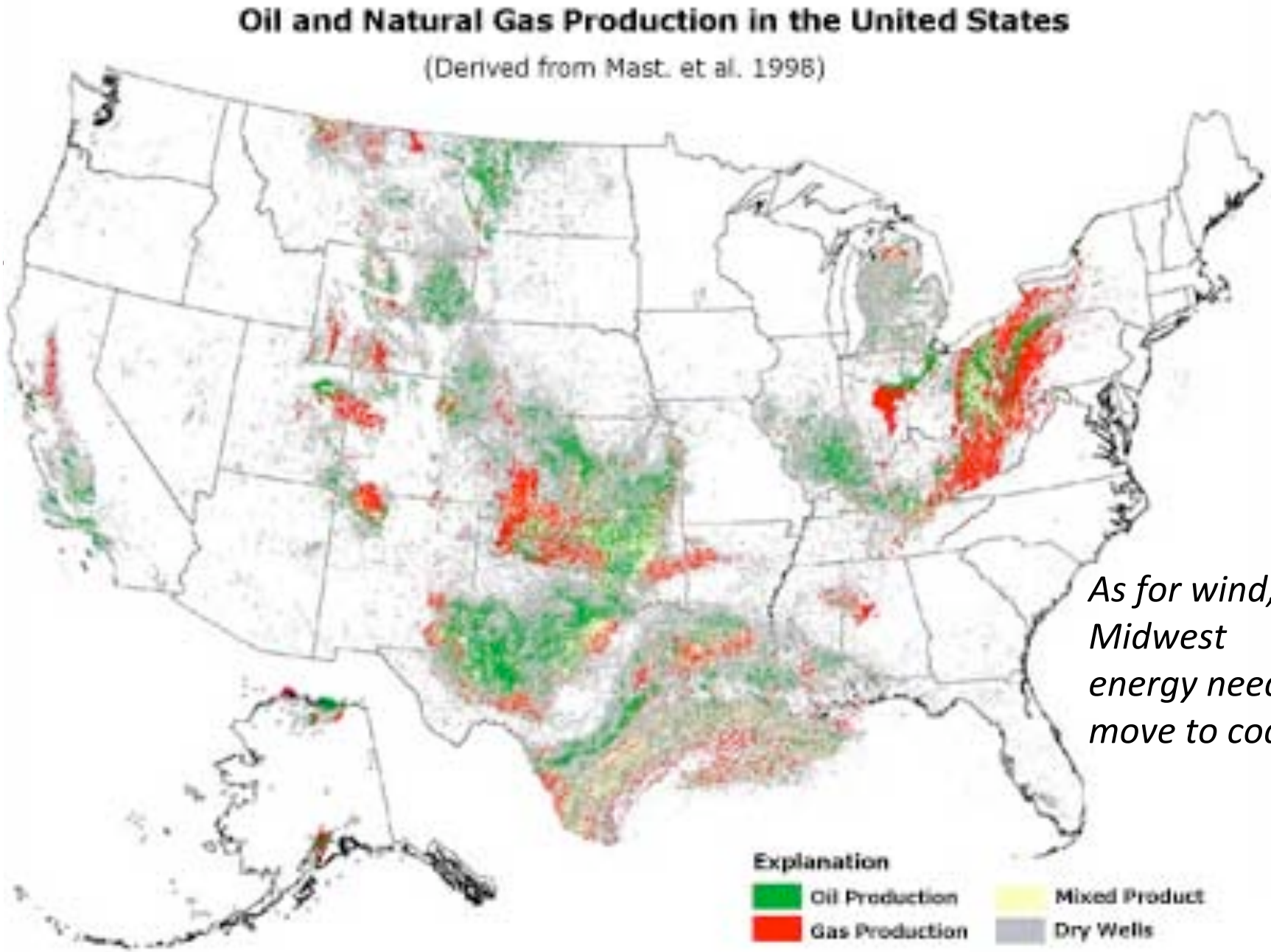
2006: Russia cuts off all gas flowing through Ukraine in dispute over prices & debts, causing shortages in European countries downstream… and interest in trans-Caspian pipelines.

Proposed trans-Caspian routes would bypass Russia

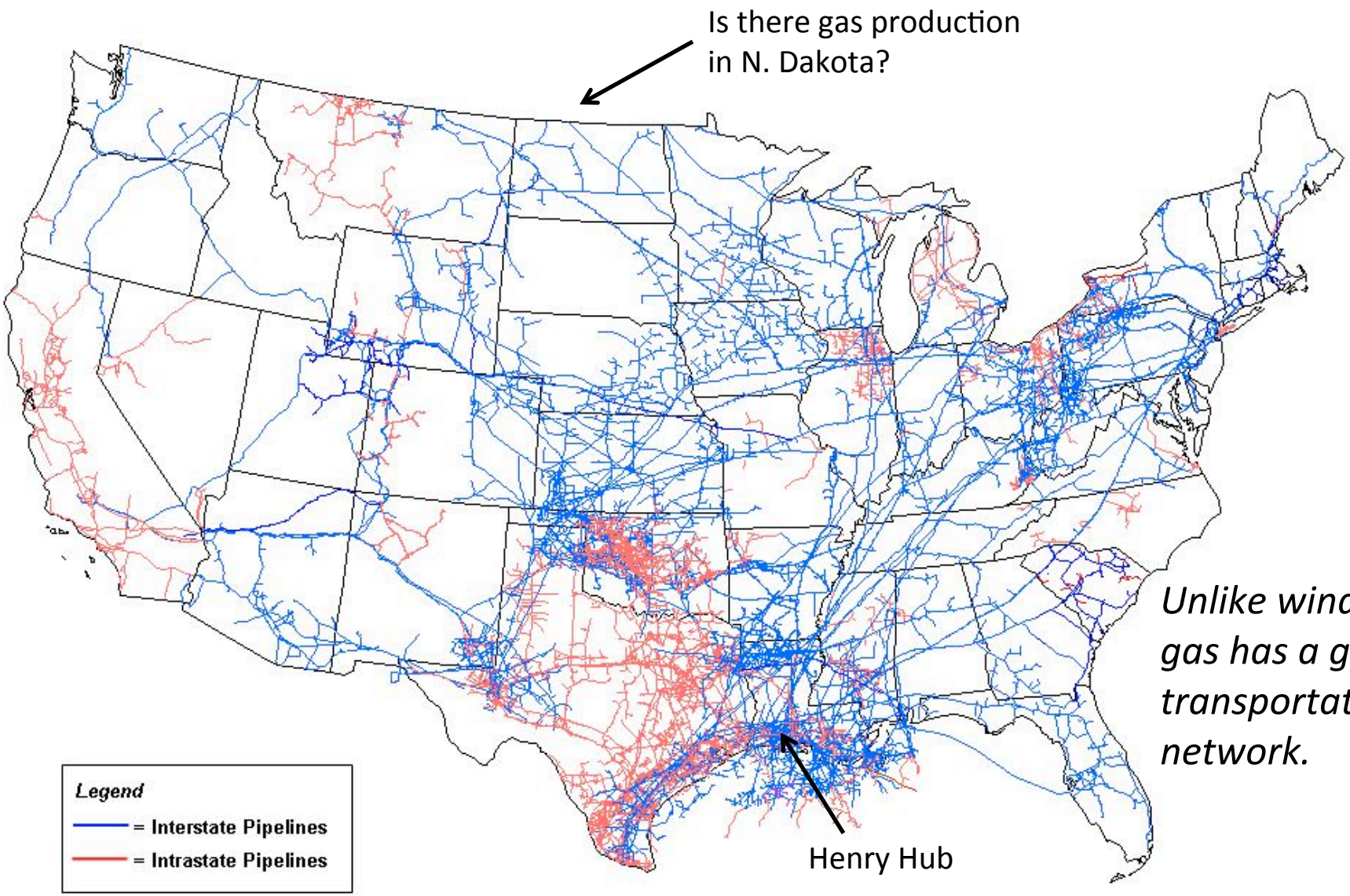
Pathway to bring gas from Turkmenistan, Kazakhstan oil and gas to Europe. Kashagan oil field in Kazakhstan is richest find in 30 years. *Figure: from Japanfocus.org,, source unknown*

Natural gas production in U.S. is not near major demand



As for wind, Midwest energy needs to move to coasts

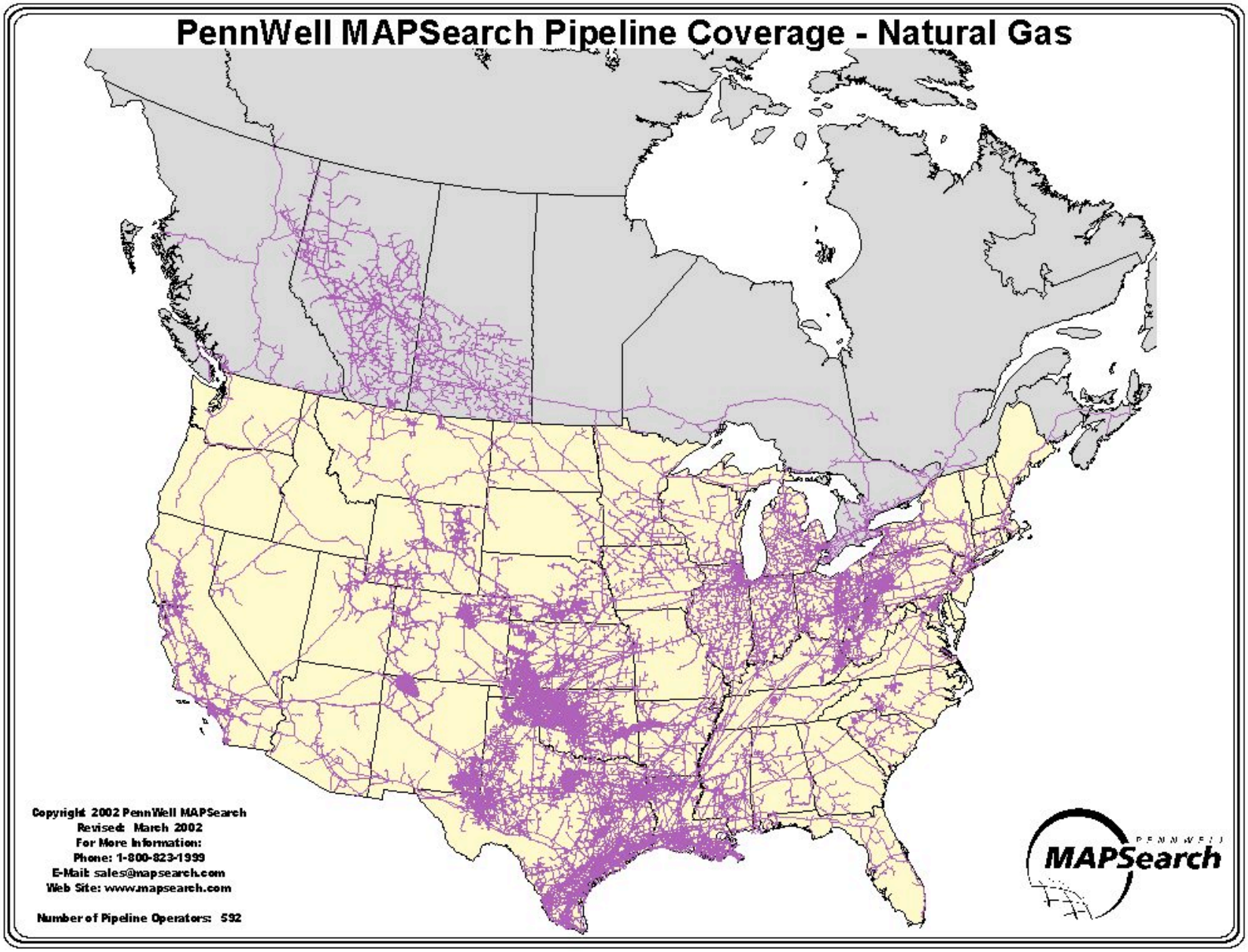
Again prompts pipeline network to move gas to demand



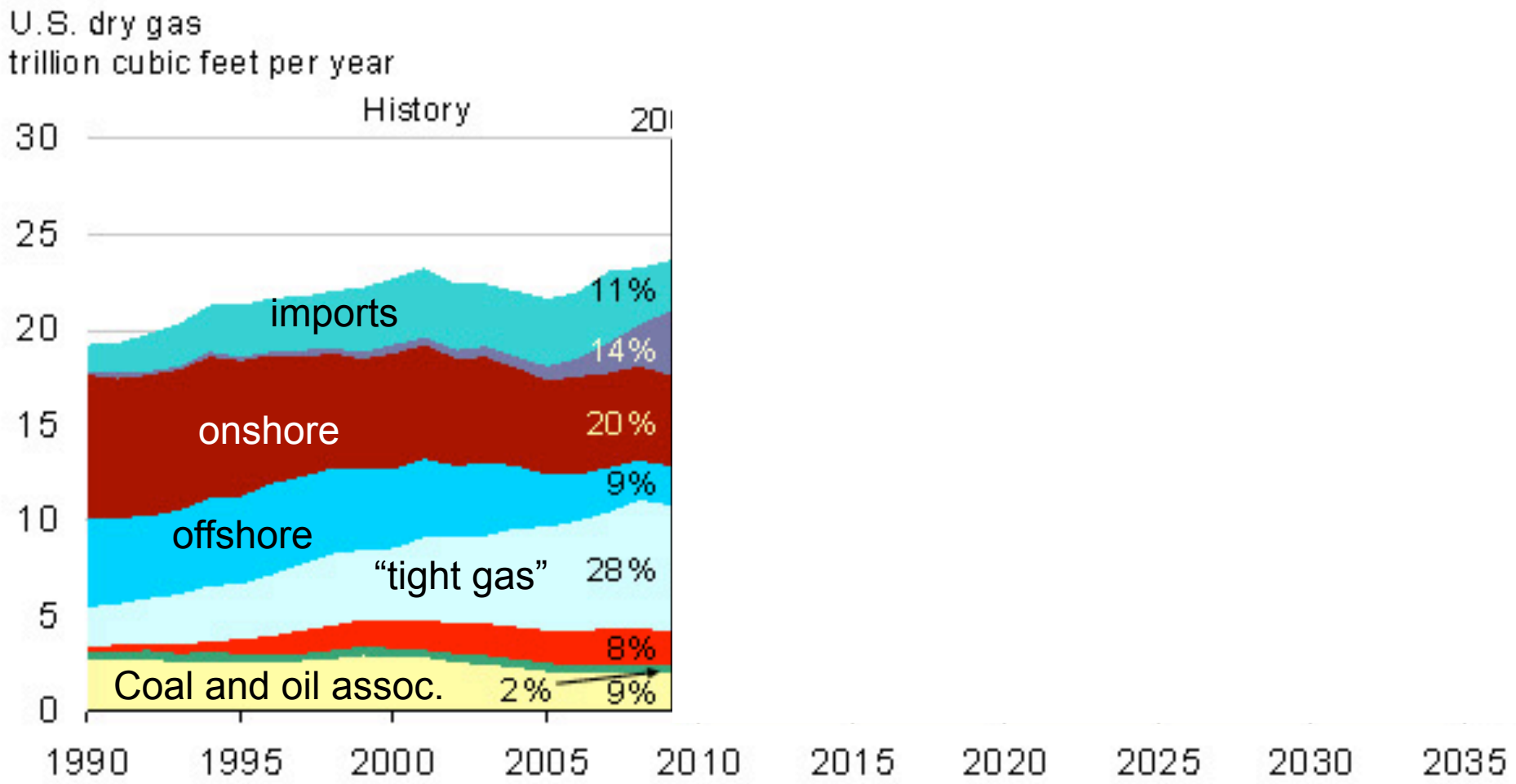
Unlike wind, gas has a good transportation network.

Source: Energy Information Administration, Office of Oil & Gas, Natural Gas Division, Gas Transportation Information System

Network crosses U.S. border to reach up to Alberta



Gas supply has turned to unconventional sources



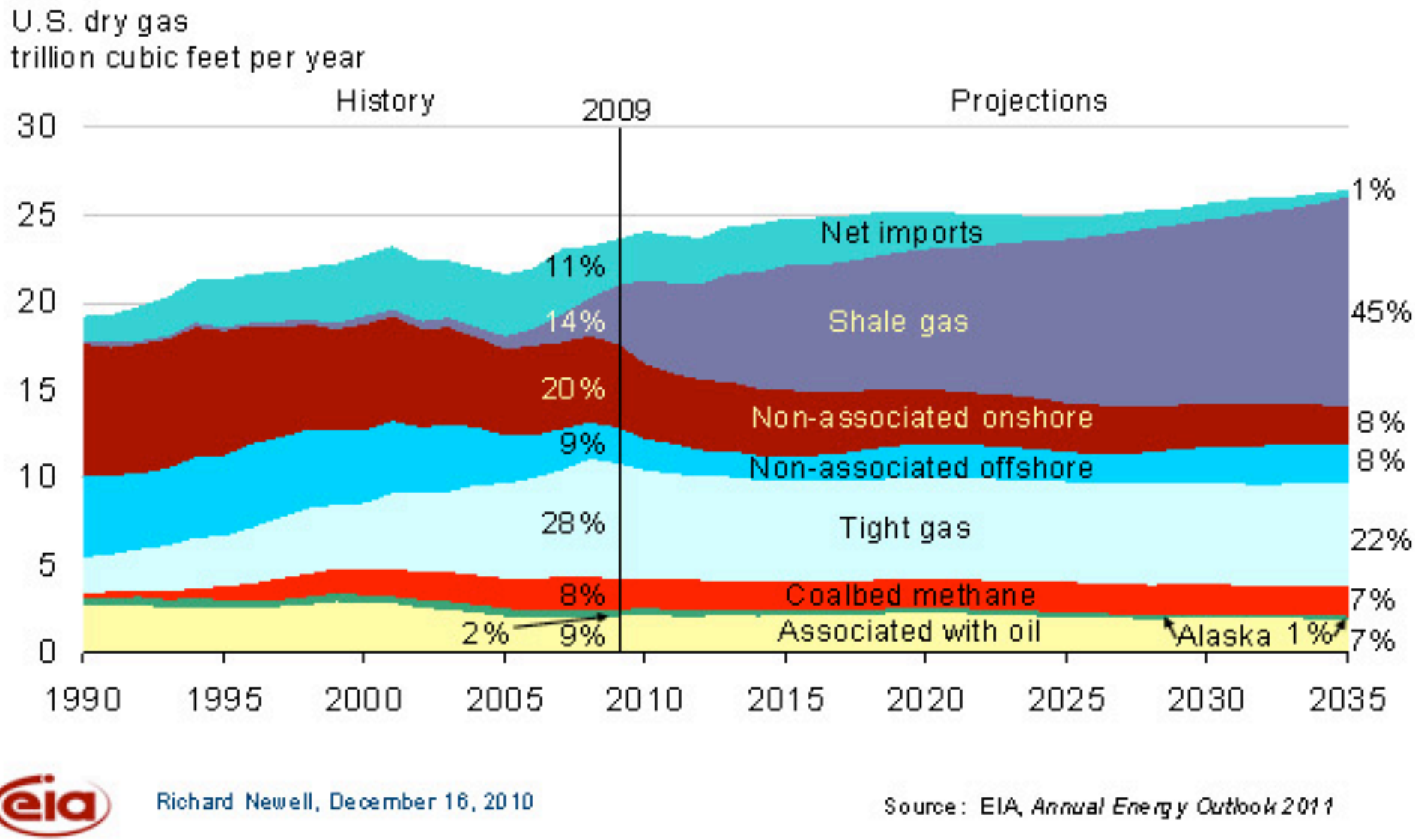
Richard Newell, December 16, 2010

Source: EIA, *Annual Energy Outlook 2011*

Note that imports projected to drop even as demand grows

Gas supply has turned to unconventional sources

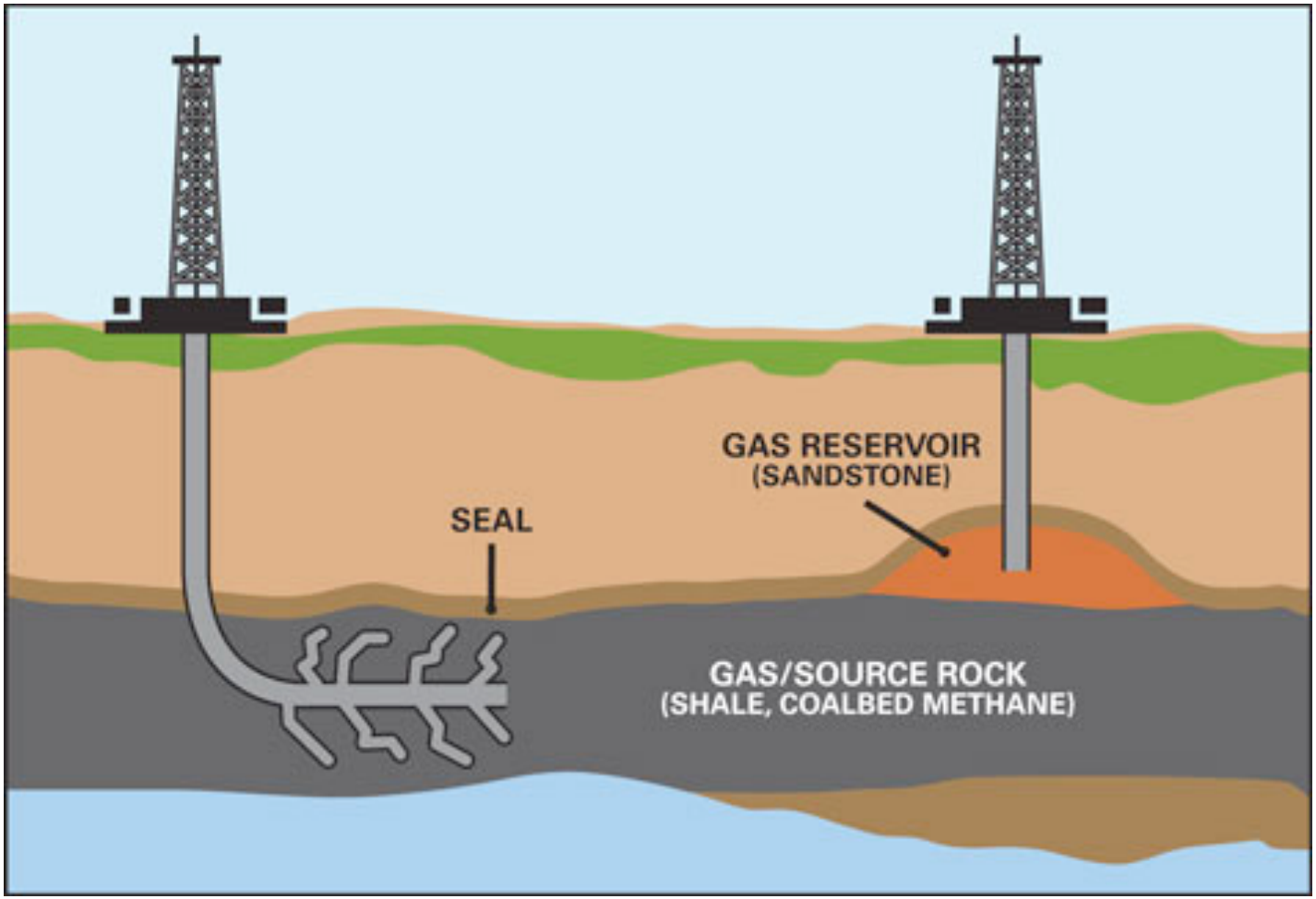
Shale gas has revolutionized U.S. energy landscape



Note that imports projected to drop even as demand grows

Fracking (hydraulic fracturing) for shale oil and gas

Allows extraction of oil and gas from rock where it wouldn't otherwise flow



Hydraulic fracturing

Conventional production

http://www.youtube.com/watch?v=nvnnBcxhzNA

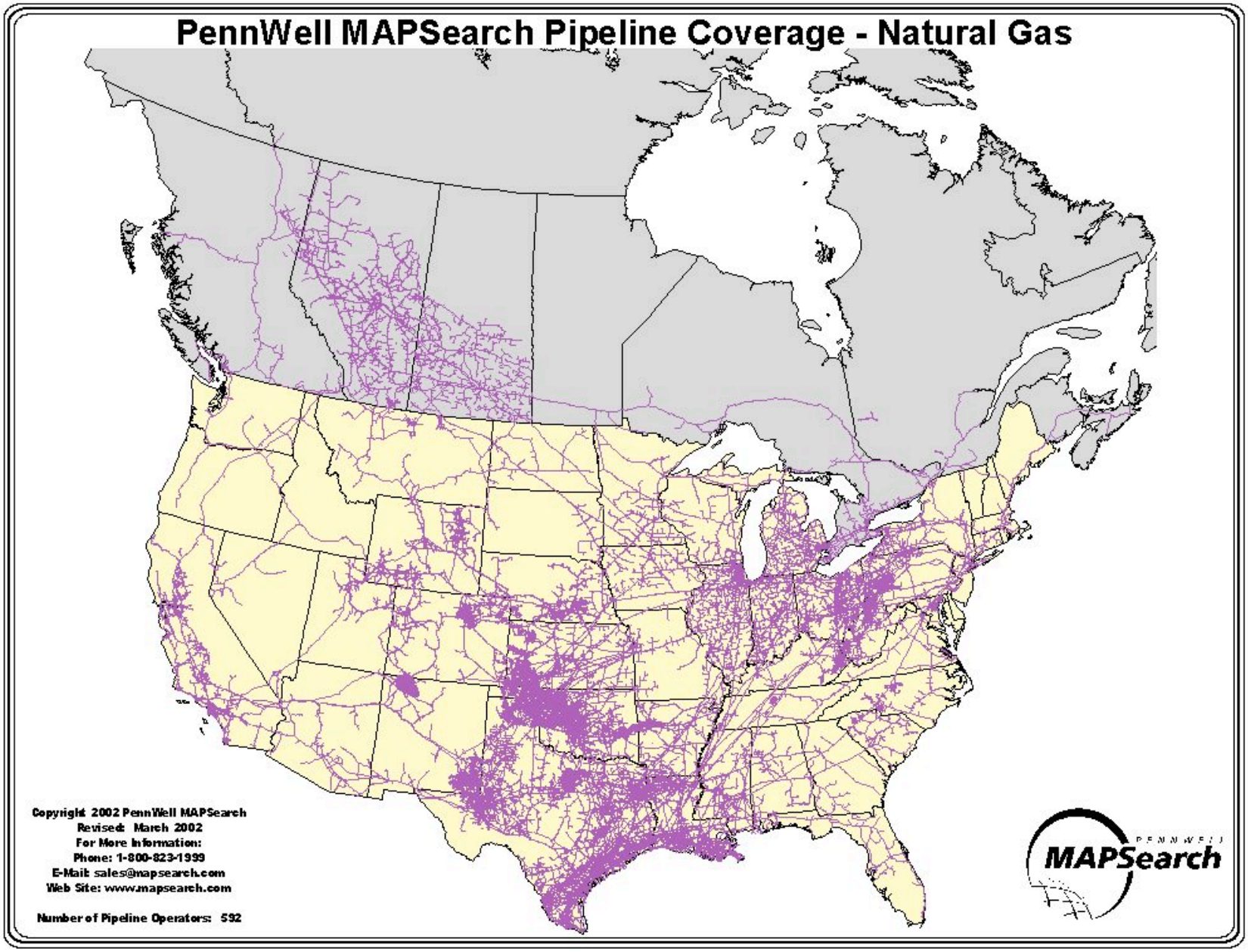
Image from Alberta Oil

Shale gas may offer relief from dependency on foreign gas

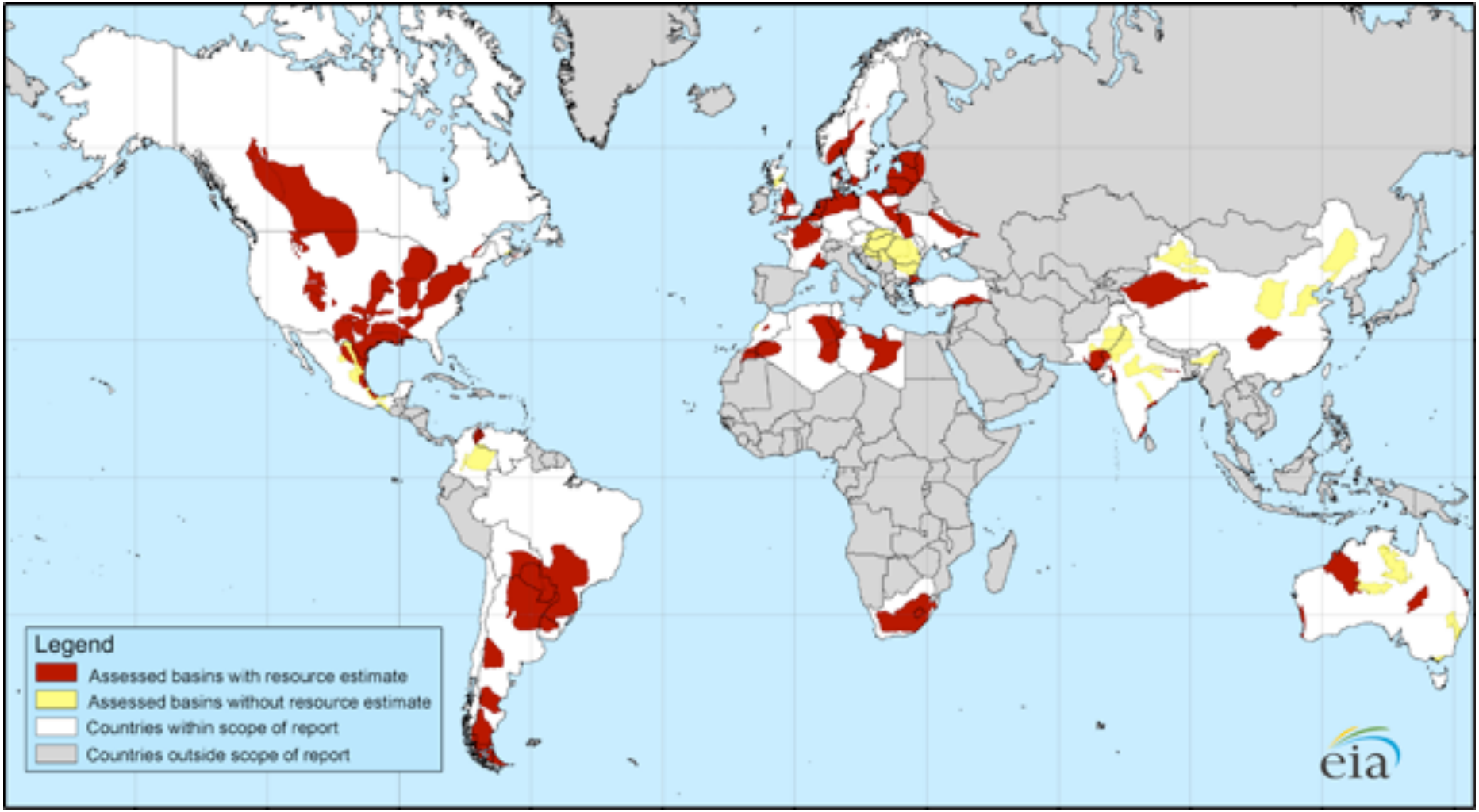
Fig. 1: North American shale gas plays

Source: Ziff Energy Group

New shale gas is near old production locations



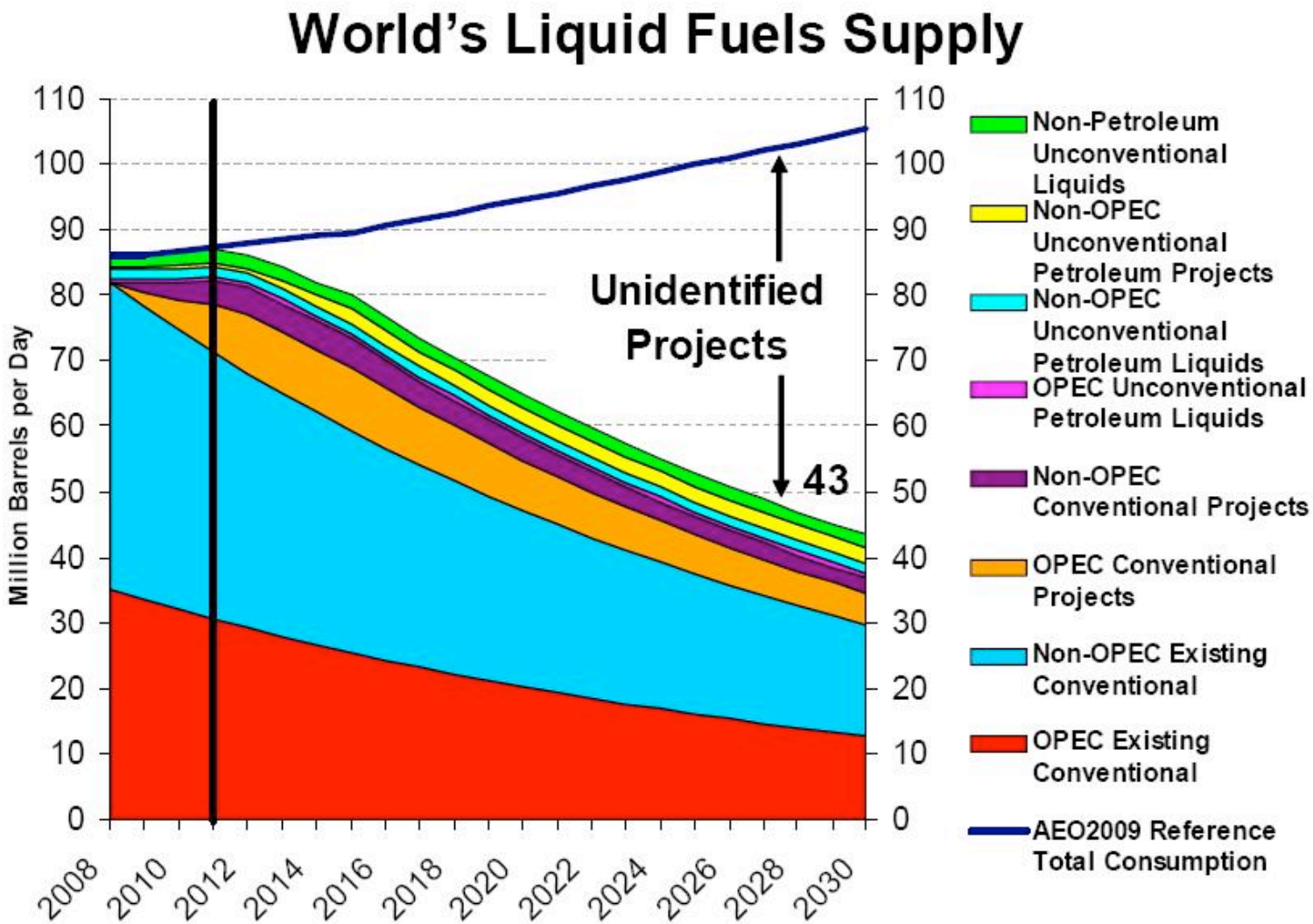
Shale gas may offer means of putting off global supply crisis



The EIA estimates that shale gas will provide 60 years of supply at 2030 consumption rate

No similar optimism for oil

we are already turning to sources less and less easy to extract



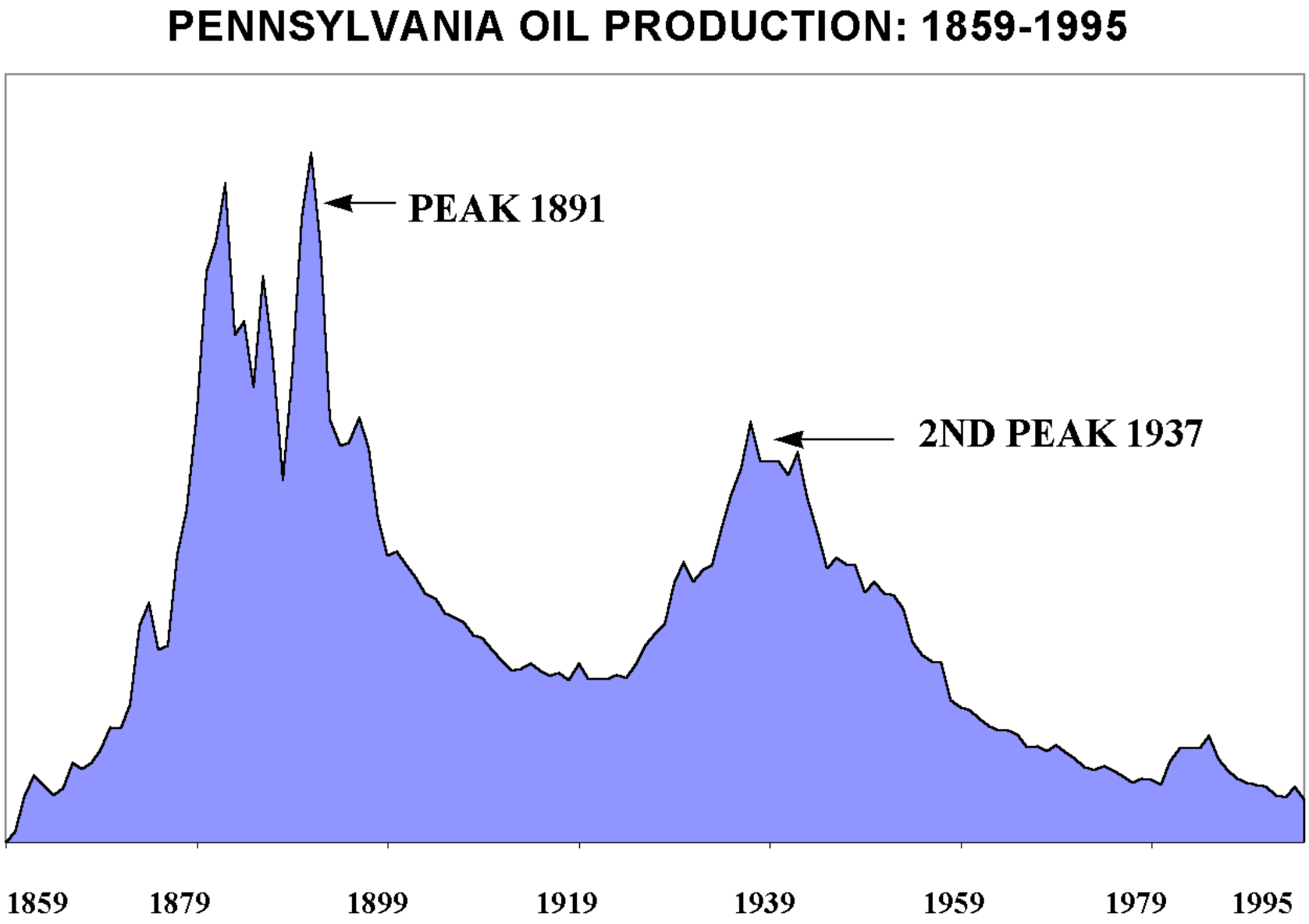
Source: EIA, AEO2009

U.S. dependence on imported oil – why?

It’s not just because we are using more and more

It’s also because we used up our domestic oil supply already

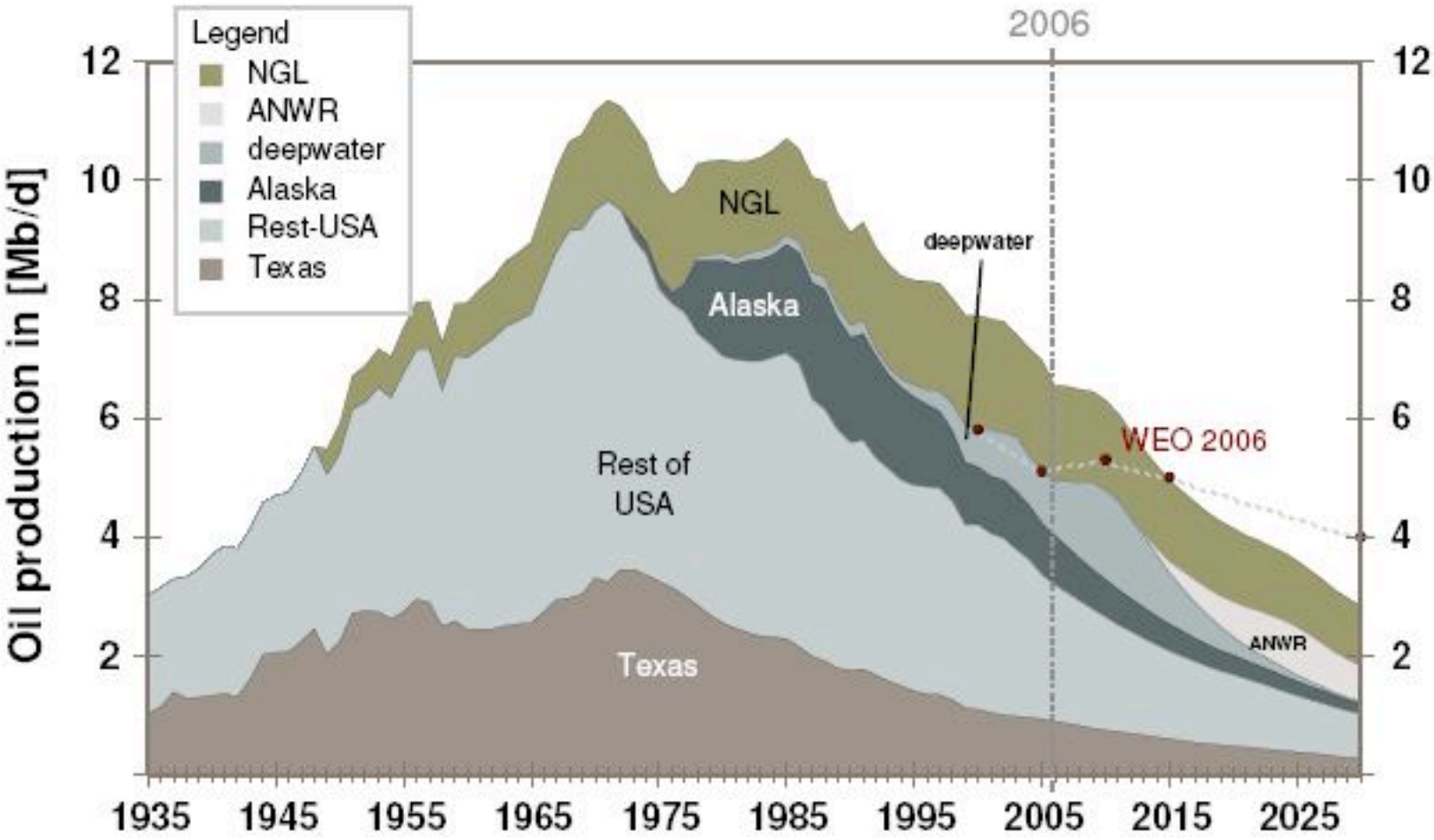
U.S. has largely run out of oil



From: R. Udall, "When will the joyride end?", 1999.

U.S. has largely run out of oil

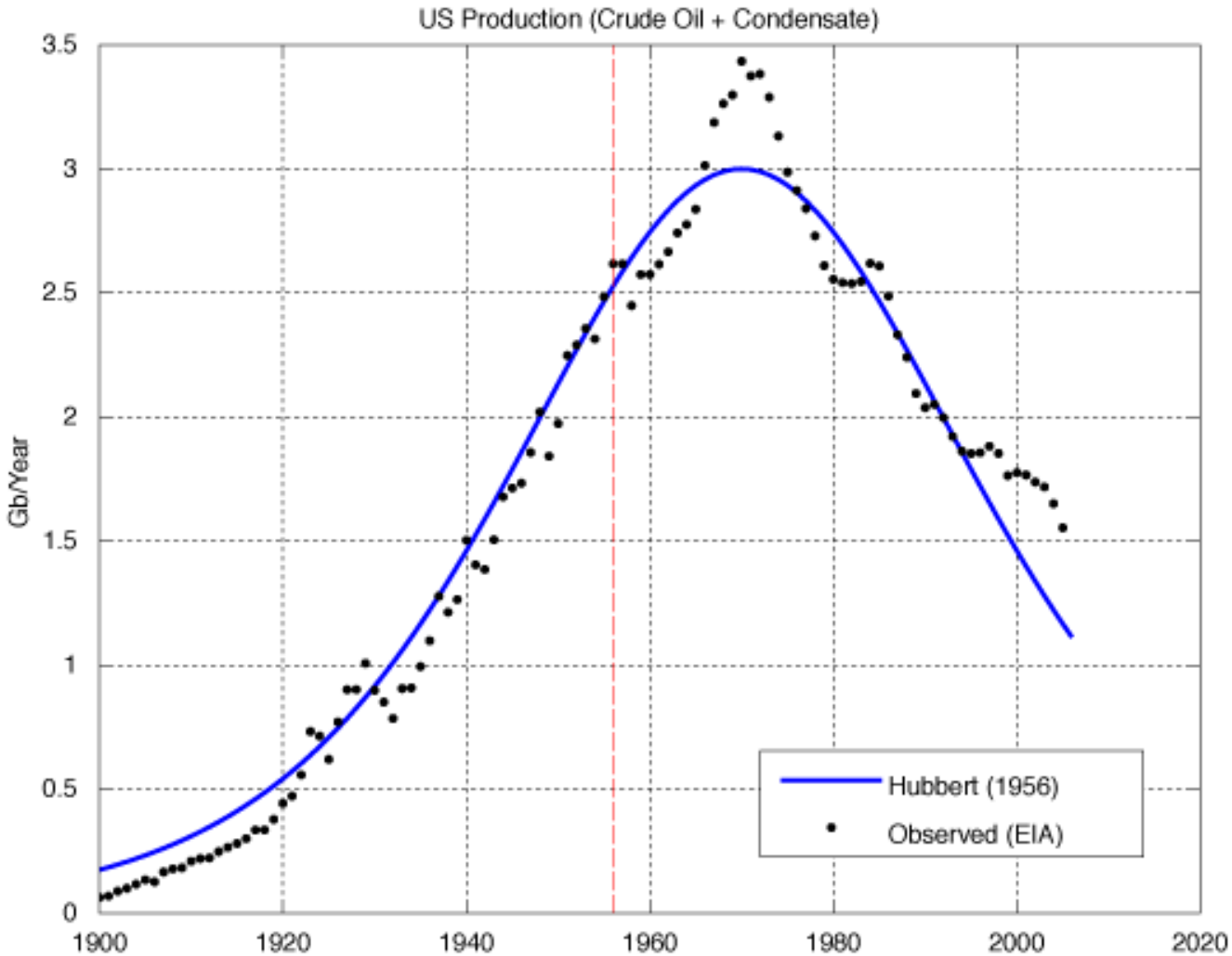
Figure 29: Oil production in the USA



From: TheOilDrum.com (original source unknown)

"Hubbert's peak"

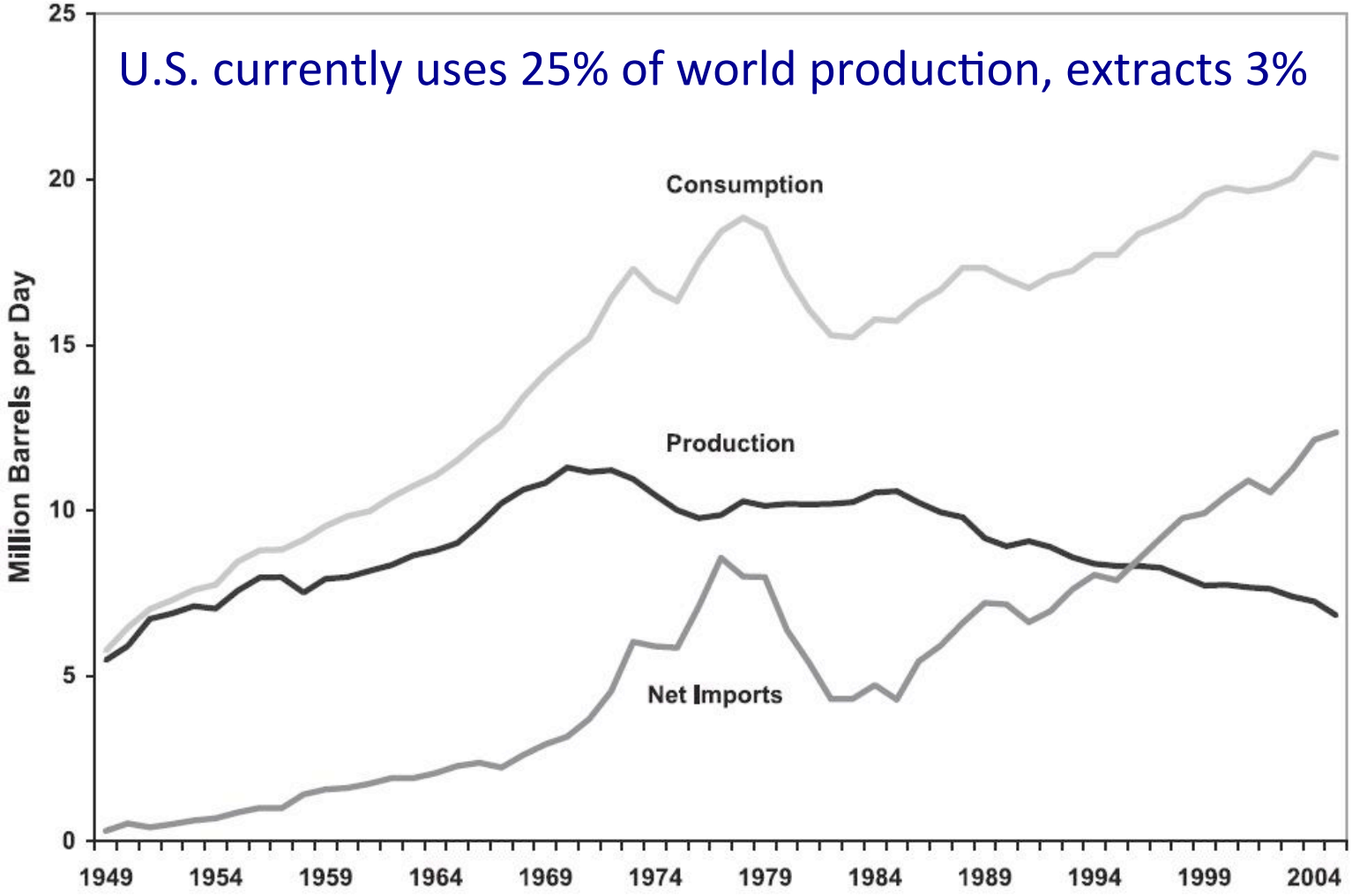
Famous prediction in 1956 by M. Hubbert, U.S. geophysicist, proven in 1970s



Data: U.S. Energy Information Agency; Image: Wikimedia Commons (S.Foucher, 2007).

Decreasing production and increasing consumption

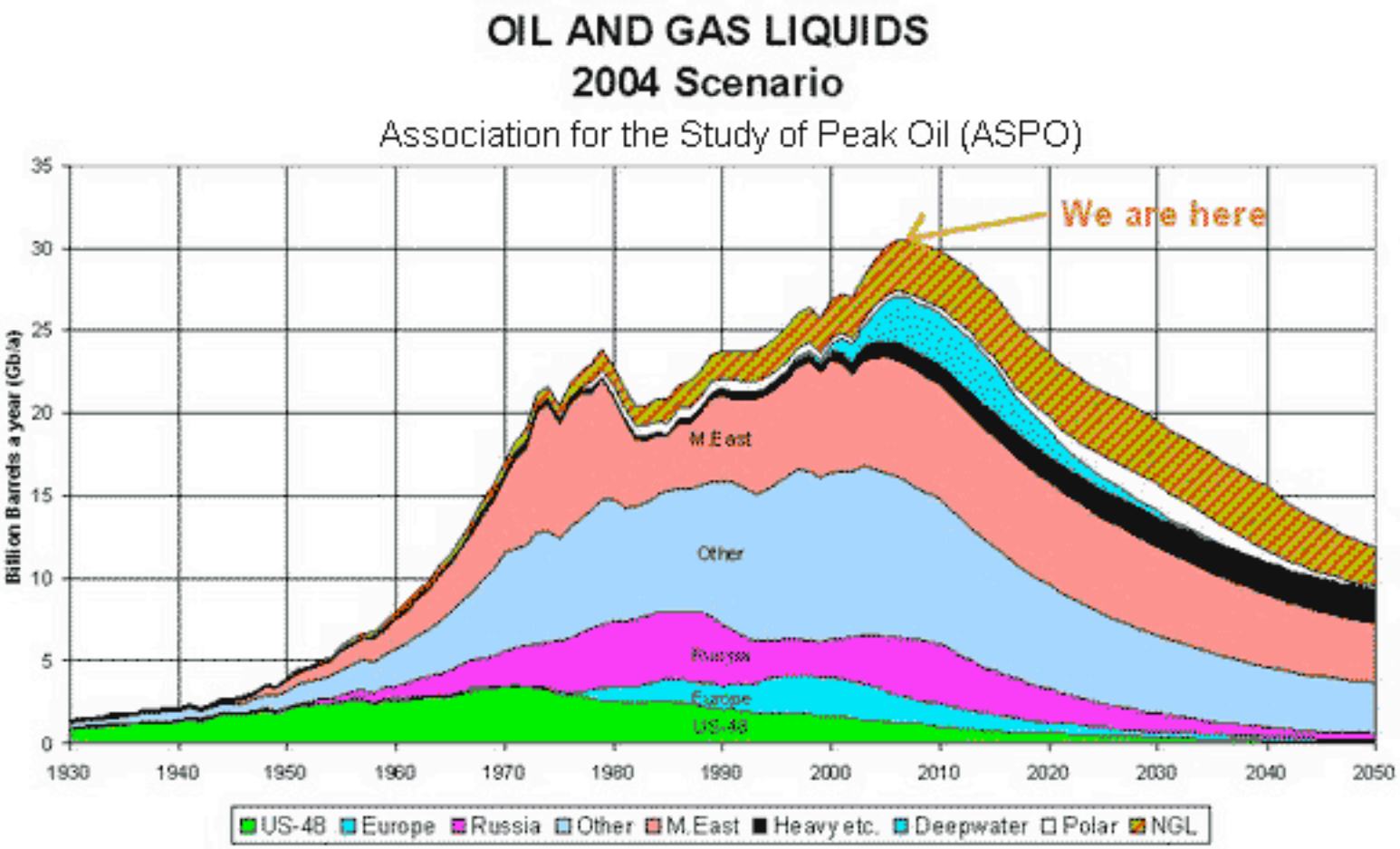
mean U.S. now dependent on imported oil



Imports are now more than twice domestic production, and rising while domestic production is falling.

From: Council of Foreign Relations, "Independent Task Force Report #58: National Security Consequences of Oil Dependency",2006.

Is entire world oil near a global Hubbert's peak?



Somewhat dubious to trust a claim that we just now happen to be at the absolute peak when no decline is yet evident…

Fossil fuel reserve sizes (proven only)

		bboe
Consumption = 33 bboe/yr	World coal	4,500
	U.S. coal	*1,100*
Consumption = 30 bboe/yr	World oil (conventional)	1,200
Consumption = 19 bboe/yr	World gas (conventional)	1,000

Growth in energy use is ~ 2 %/yr

1 barrel of oil equivalent = 6.1 GJ

Data source: EIA

Fossil fuel reserve sizes (proven only, & still uncertain)

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Consumption = 33 bboe/yr	World coal	4,500
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	World oil (w/ oil sands)	1,400
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	World oil (w/ oil sands)	1,400
	World oil (w/ shale oil)	4,000 ?
Consumption = 19 bboe/yr	World gas (conventional)	1,000
	World gas (w/ shale gas)	2,200 ?

Most of oil shale - 1400 bboe – is in Green River Shale

Growth in energy use is ~ 2 %/yr

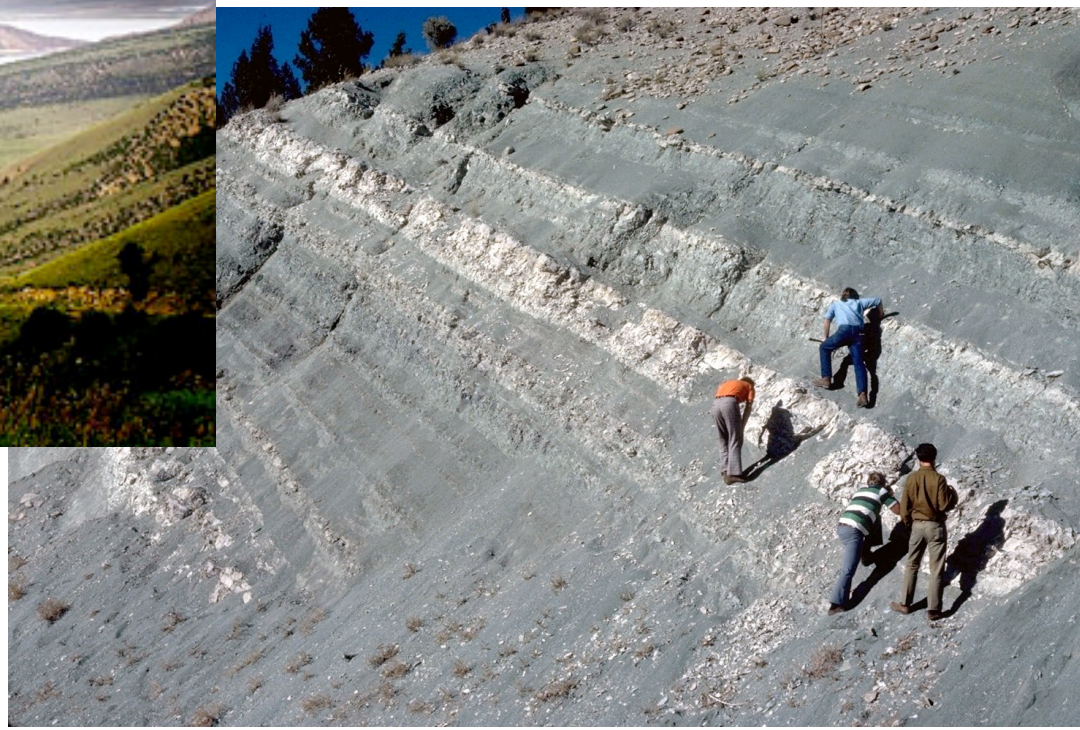
1 barrel of oil equivalent = 6.1 GJ

Data source: EIA

Would we accept digging up/fracking the Green River shale?

Green River winds through Dinosaur National Monument, Canyonlands National Park

Flaming Gorge recreational area, Utah
Image: from National Forest Law blog, source unknown



Green River shale in roadcut
Image: Bruce Simonson, Oberlin College

Alternative: make liquid fuel from abundant U.S. coal instead?

We have a long history of producing ***gas*** from coal.

"Coal gas" (mostly methane) was originally byproduct of coal processing to coke..

….then manufactured & widely used in 1800s for lighting (+ cooking and heating).

Why not also try to make *liquids* from coal?

… because it takes a lot of energy to do so.

Gaslamps = symbol of Victorian melodrama

Fossil fuels: another conundrum

If we run out of oil, but have enough coal, we can keep our transportation system running by liquifying it

….but only at price of making climate change and damages worse

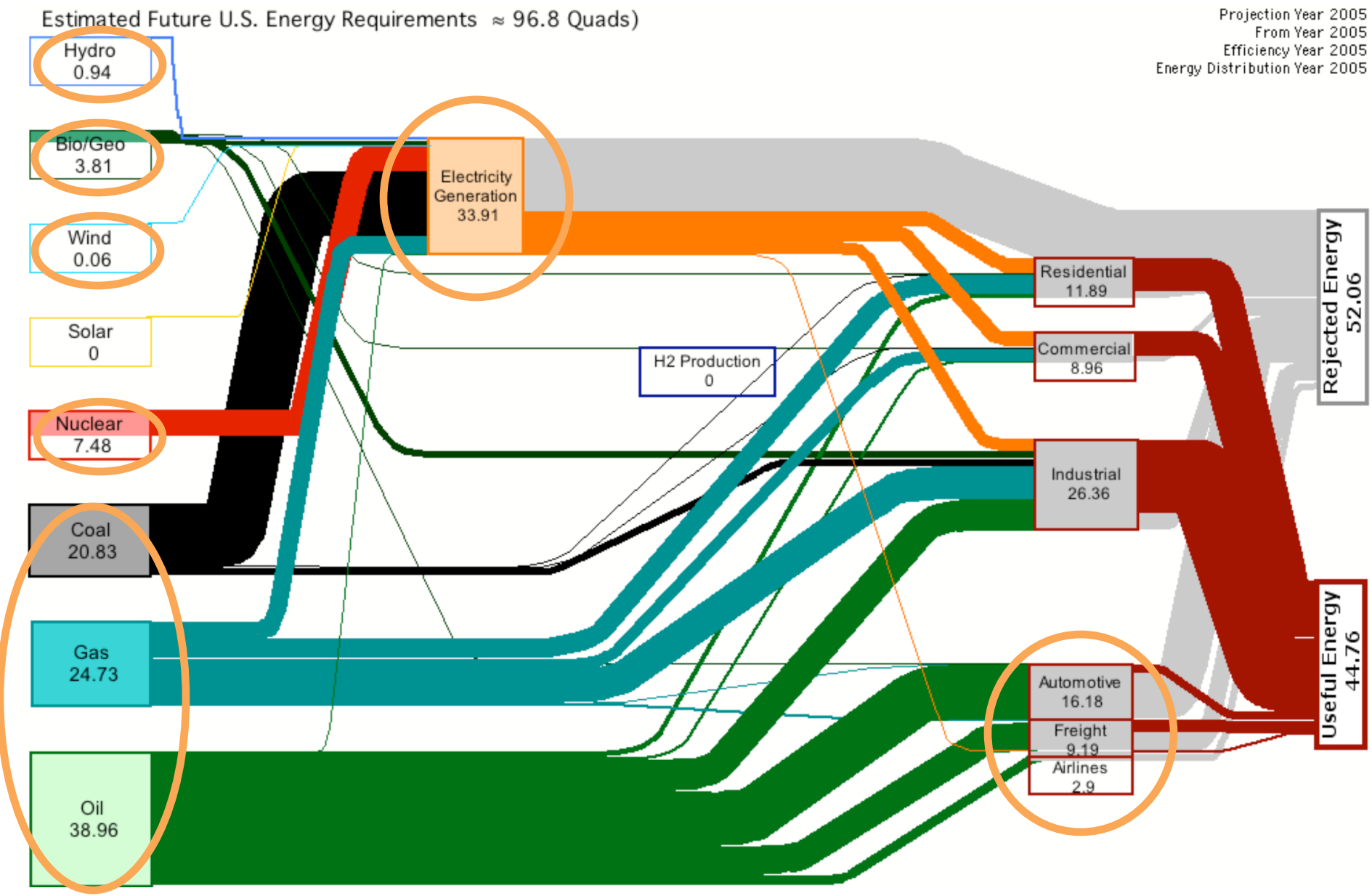
The environmental impacts of extracting unconventional oil are bad enough, but a bigger concern is accelerating climate change

need to consider energy cost of conversion to determine how bad

What we've covered so far, and what's left out

U.S. energy use, 2005

from LLNL, in quads/yr : 1 Q / yr ~ 10^{18} J / yr ~ 30 GW



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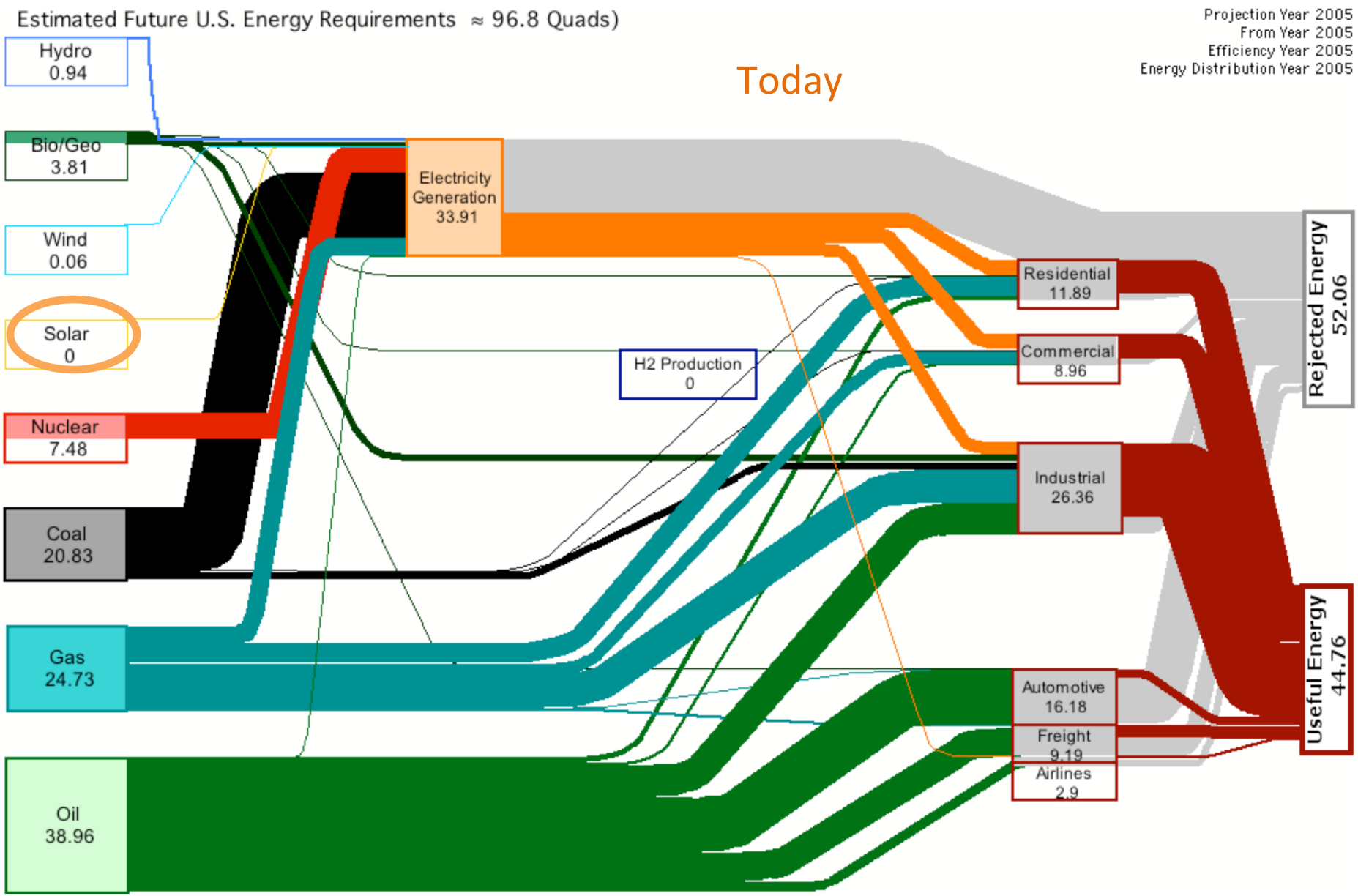

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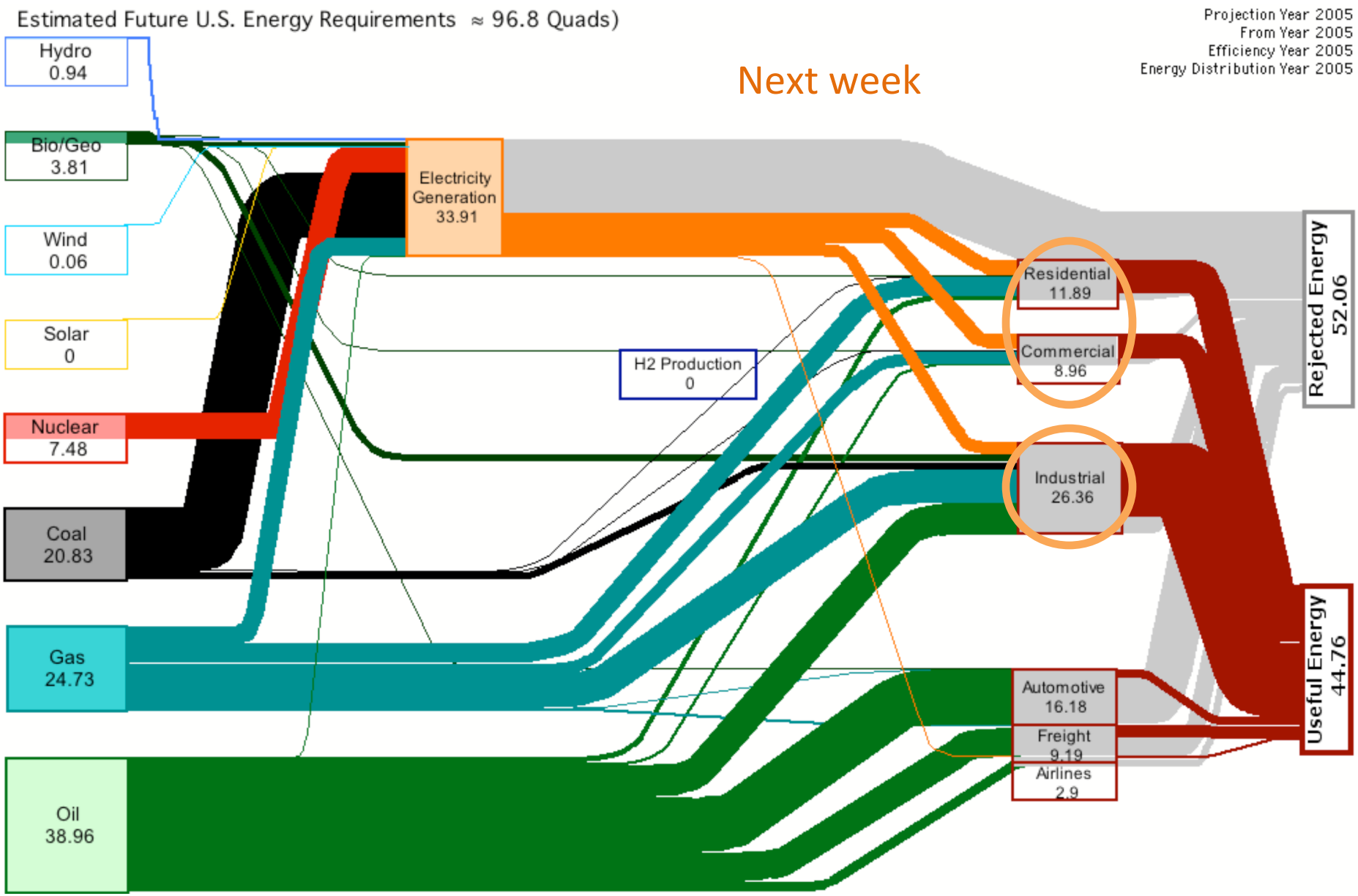


Solar intro (very brief)

Two main energy conversions using sunlight are both called "solar"

- **Solar thermal** – use mirrors to concentrate sun and heat something and drive a heat engine, which then turns a generator and makes electricity

- **Solar photovoltaic** – convert sunlight -> electricity directly in a semiconductor via the photoelectric effect.

Solar thermal: just uses heat from sun (advantage is that you can build a better heat engine than the atmosphere)

2 of 9 (354 MW total) SEGS parabolic trough solar thermal installations in Barstow, California, starting 1984, built by Luz Int. …which went bankrupt. Still operational.

Solar thermal advantages: Proven technology (steam turbines) + heat is store-able + no exotic materials

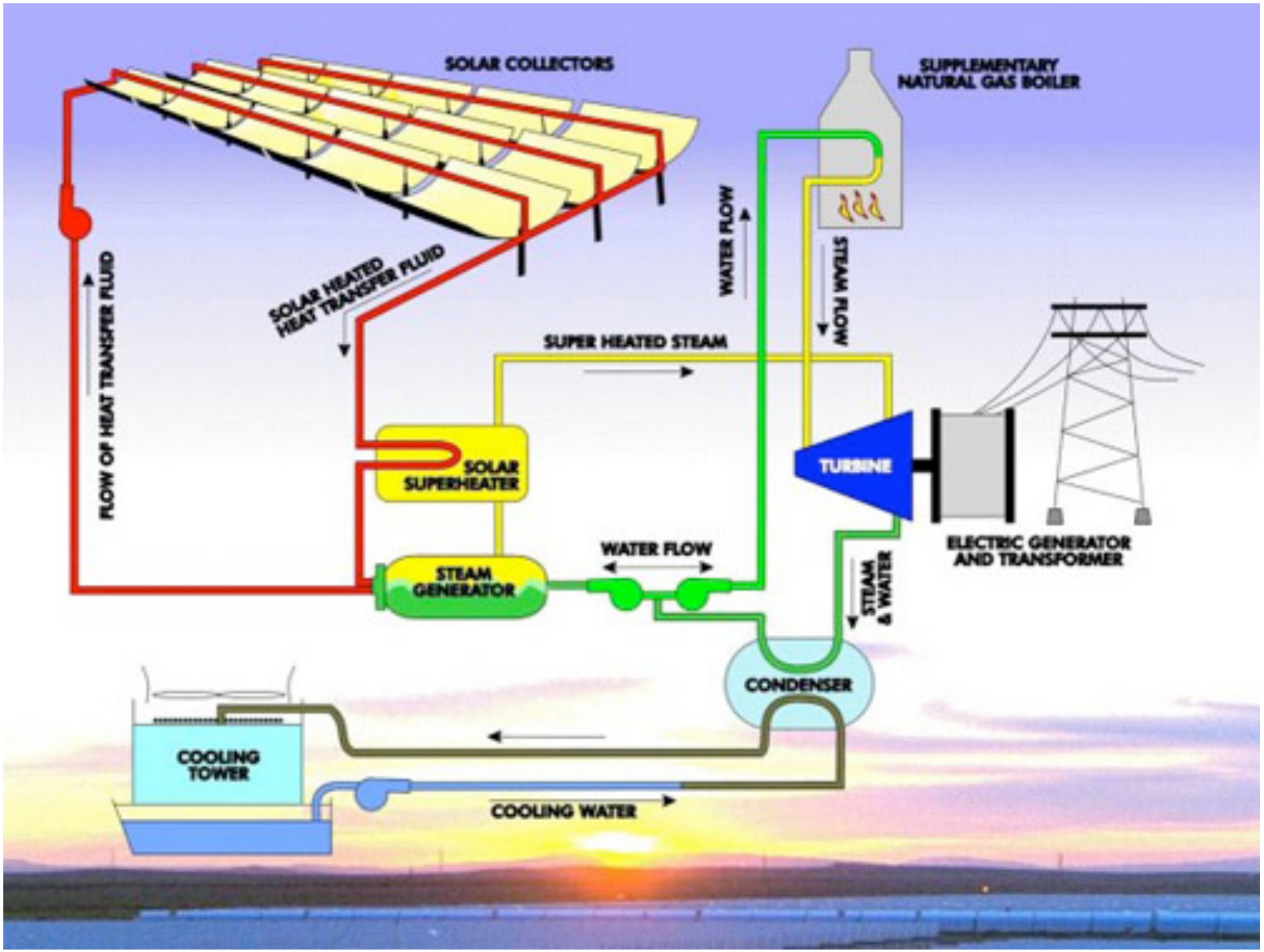


Diagram: source unknown (from the Green Technology Blog)

Power towers aim for higher efficiency

By concentrating bigger mirror area on central tower, can produce hotter temperatures and so higher Carnot limit

11 MW solar thermal PS10 "power tower" in Seville, Spain
(govt. subsidized by 27 euro cents/kWh)

Power towers aim for higher efficiency (higher T)

BrightSource Solar Two power tower, near Barstow, CA. Ivanpah (400 MW capacity) is being built in Mojave now at $2.2 B cost: $5.5/W install cost. Capacity factor = ?? %. Possibly can run near full capacity with storage. CA has 33% RPS standard

Can solar thermal ever be cost-competitive?

Solar thermal is far more expensive than fossil fuel generation, by factors of at least 2, likely more (costs uncertain)

Estimates of cost breakdown

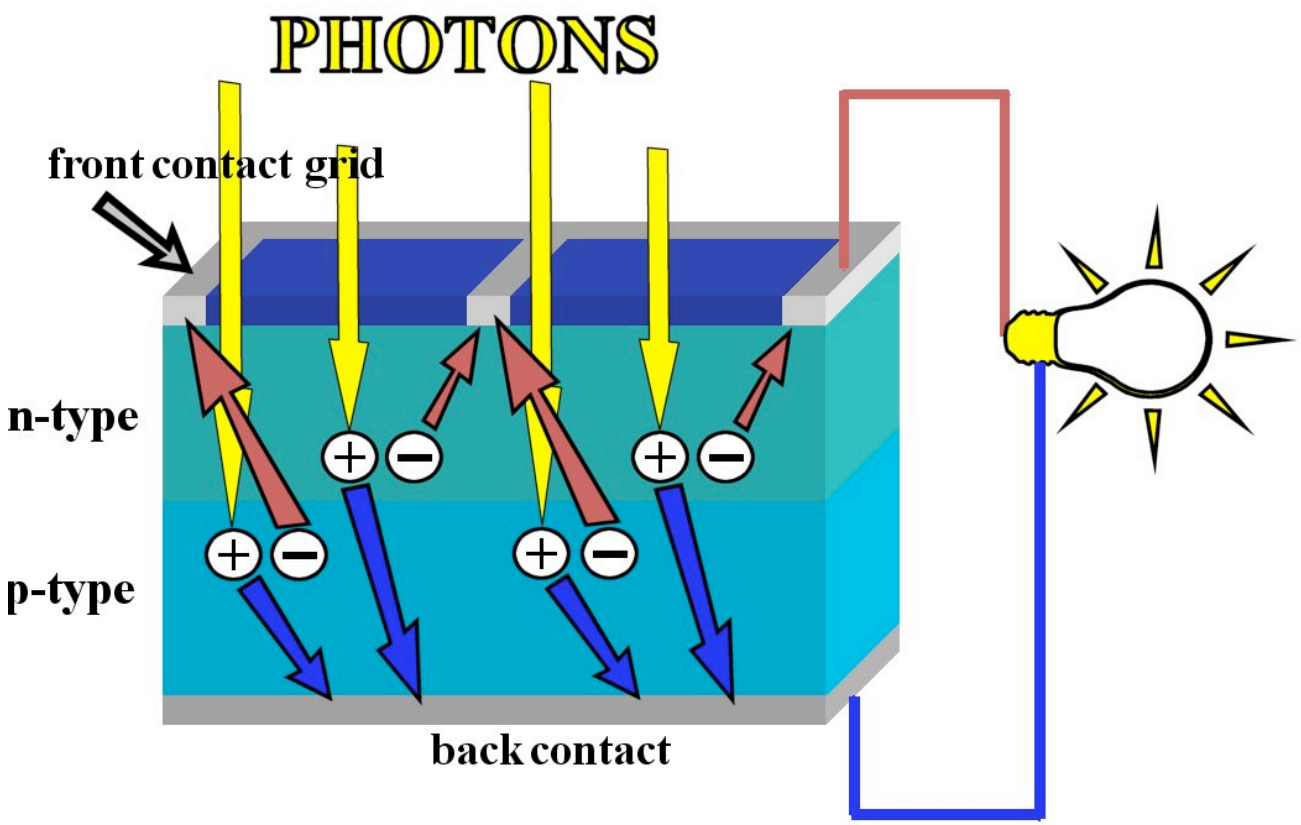
- Glass mirrors: 16-24% of cost (typically metal on glass)
- Support structure: 35-50%

Mirrors + structure = 50% of cost for dish or heliostats (tower)
= 75% of cost for trough.
Mirrors are expensive for high broadband reflectivity

- Receiver/turbine: 13-17%
- Tracking: 20-24%
- Control: 1%

Source: Ashvin Shah, Estimated Costs of Solar Thermal and Electrical Energy, August 1999

Solar photovoltaic – skip mechanical step entirely and go directly from radiation to electricity – *no turbine, no generator*

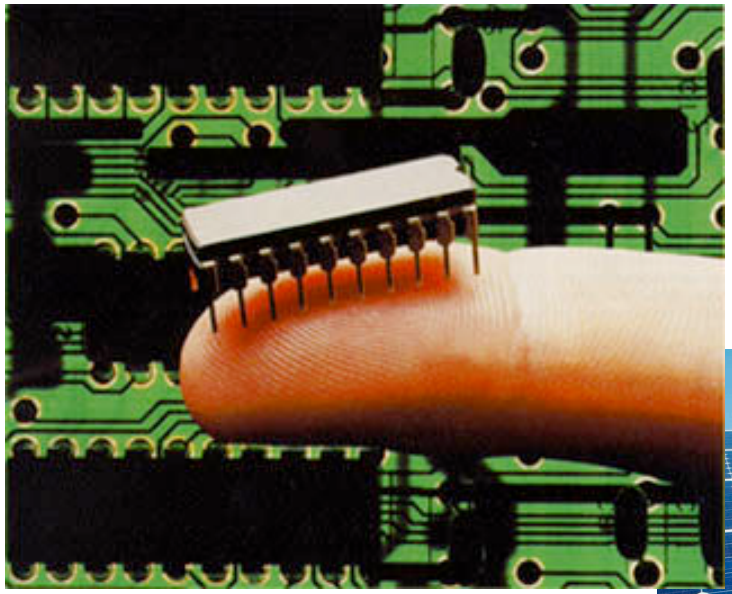


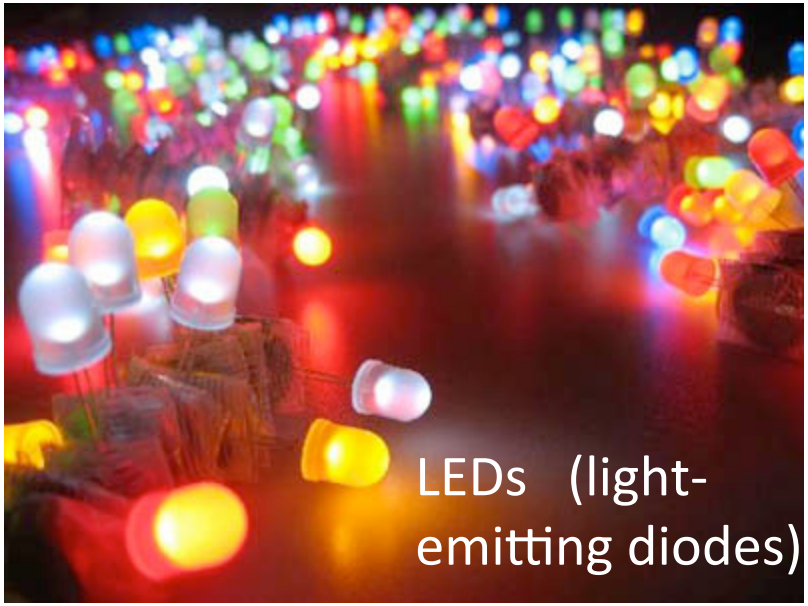
Photoelectric effect produces free electrons in semiconductor material. Current flows if given an extra conductive path. Necessarily produces DC – current flows in one direction only. Voltages typically low.

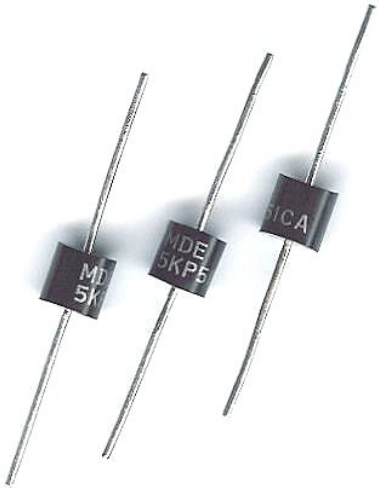
What is new in the energy field?

Semiconductors

Transistors

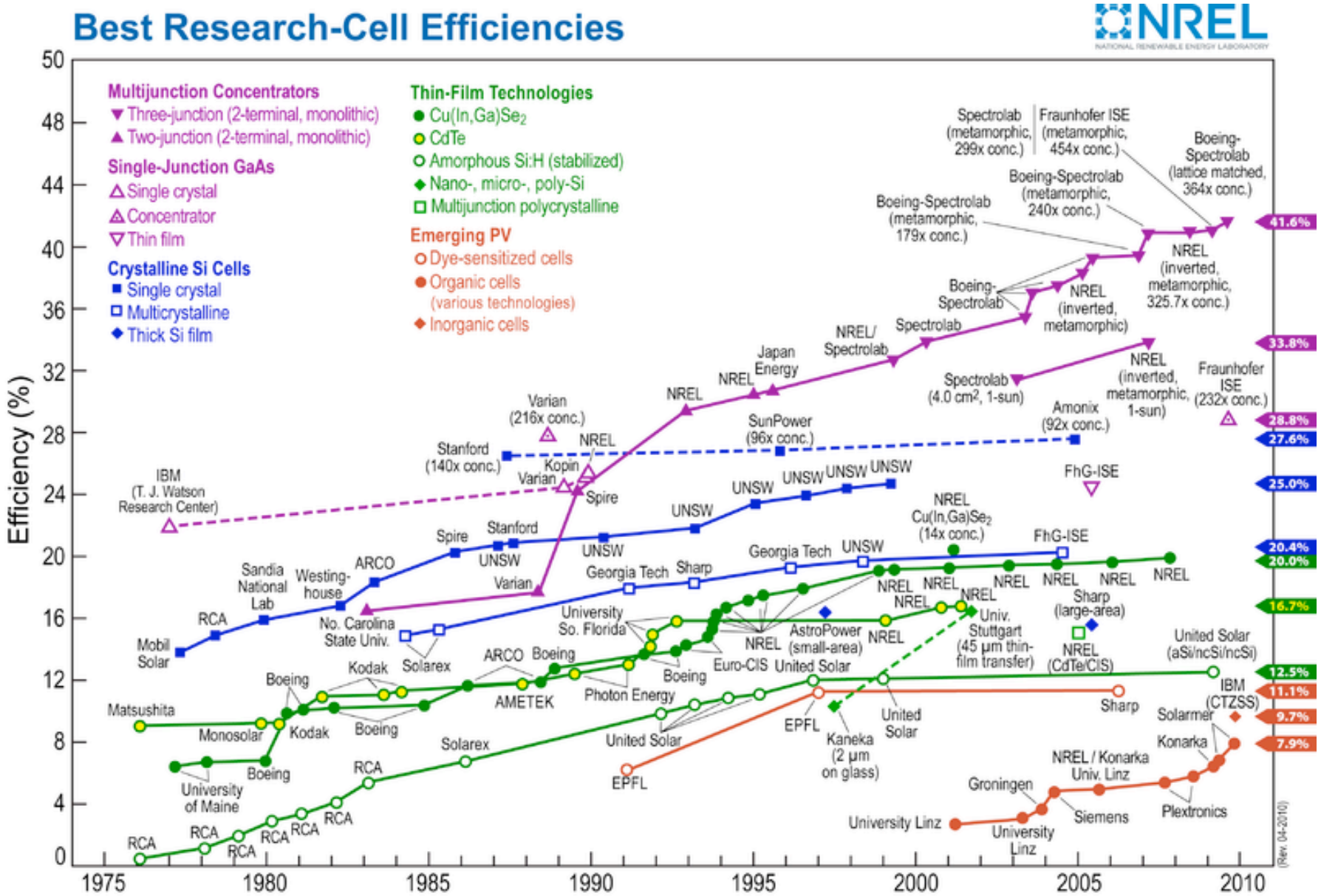






Diodes

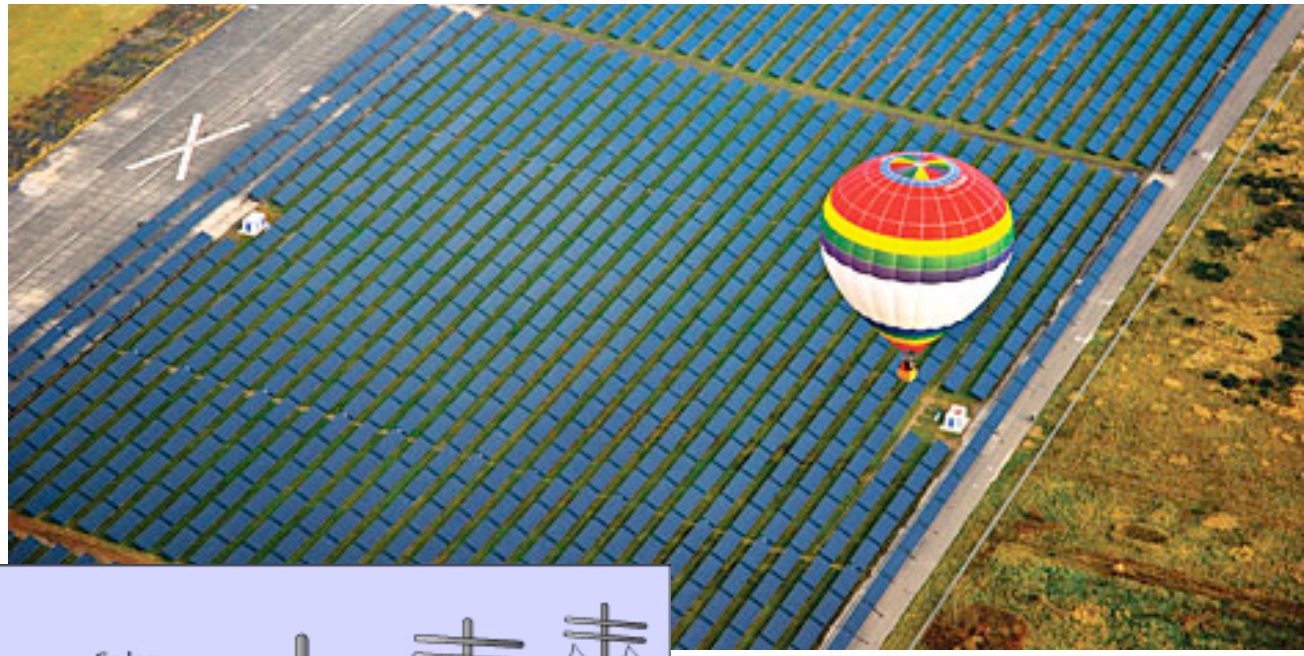
Solar PV efficiencies: up to > 40% laboratory, 10-15% commercial



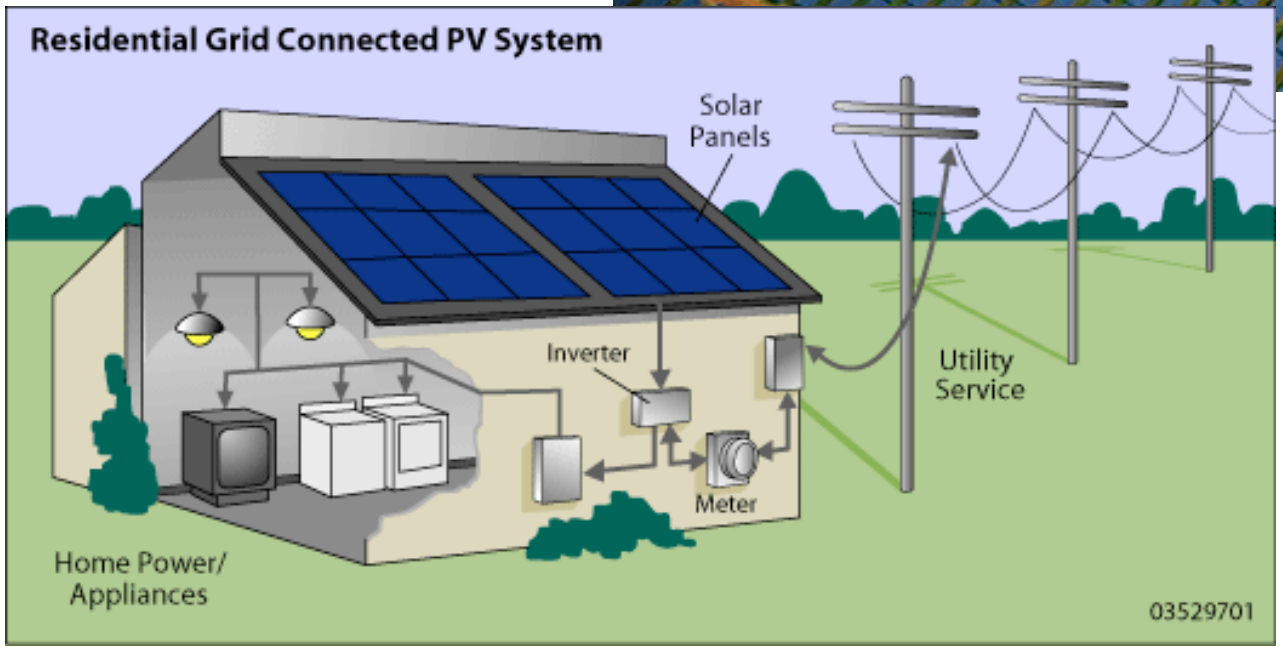
Efficiency not everything; “Thin-film cells are less efficient but cheaper

Solar PV is somewhat scale-independent

can be installed in small or large facilities (x2 cost diff.)



Residential installation typical size 1 kW. Each requires its own inverter



40 MW solar PV farm, Brandis, Germany, built by First Solar, CdTe / CdS on glass (2nd generation cells). Effective subsidy up to 45 euro cents/kWh (subsidy is 10x cost of coal-fired power)

Main barrier to use of solar photovoltaic is economics

Cost of solar panel itself appears cheap at ~ \$1 / W_p (2010 prices)
But, typical install costs (utility scale) are \$2.50-3.50 / W_p
(and costs may be low because of dumping from Chinese mfctrs.)
(note that residential installations are > \$6/W_p)

And be careful of advertised power! $W_p \neq W_{actual}$

As with wind, solar PV powers are given at some putative peak insolation (1000 W/m^2), not the actual conditions a panel encounters.

Average insolation is only 200 W/m2
So output is ~1/5 of peak power

Install price then becomes ~ \$12-18/W_{actual}

Can't compete with fossil fuel generation even when fuel is free
Cost per energy ~ \$135-245/MWh (depends also on location)

Main barrier to use of solar photovoltaic is economics

Solar panels are more efficient at using sun's energy than is wind…
but are more expensive anyway.

Three Lessons:

1. *Efficiency isn't everything in choosing technology*
2. *For solar, install cost driven by wiring more than panel cost.*
3.. *For solar, high efficiency important mostly if lowers install cost*

Other problems with solar PV

DC-AC conversion
- added expense

Not near demand
- transmission costs

Intermittency / storage
- added cost for society – harder to store electricity than heat (as in solar thermal)

Costs may rise if scale up
- materials limitations may be prohibitive

Another problem with solar PV: exotic materials needs

Crystalline Si: purified silicon + silver
Dopants: boron, gallium, arsenic, antimony
Thin-film CdTe: cadmium, tellurium
Thin-film Cu: indium, selenium, gallium

NREL projection: 20 GW/yr of new solar PV build (500 GW over lifetime, meeting the U.S.-only electricity needs), would use ½ extractable total by 2060.

NREL, "PV Facts"

Exotic materials needs in general for alternative energy

Crystalline Si: purified silicon + silver
Dopants: boron, gallium, arsenic, antimony
Thin-film CdTe: cadmium, tellurium
Thin-film Cu: indium, selenium, gallium

Batteries: cadmium, lithium
Magnets / generation: neodynium
Nuclear power: uranium

Critical limitations in elements if much alternative energy scaled up

For scale-up of:

Nuclear power

Solar PV

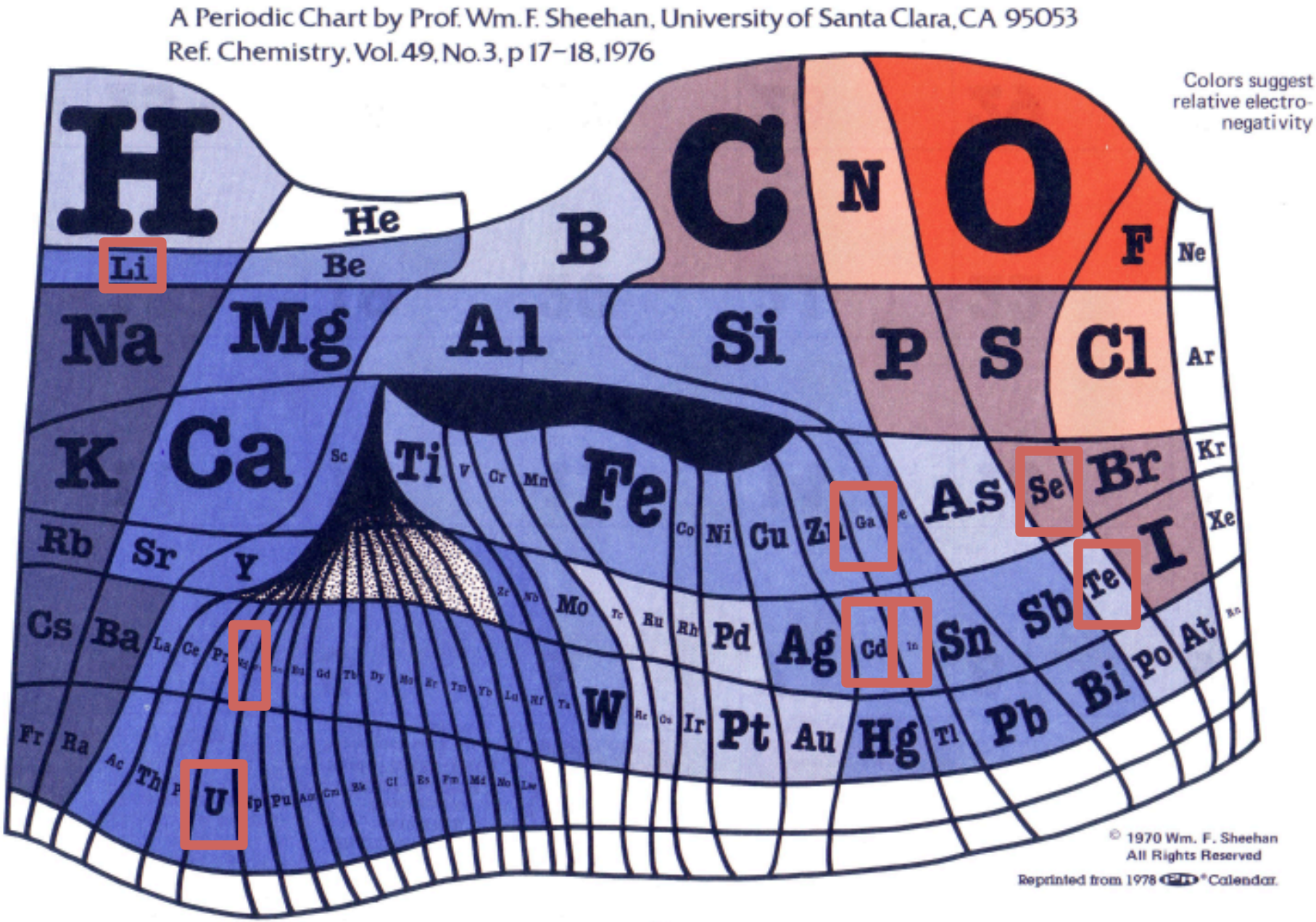
PM generators in wind

Electrification of transportation

hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
**Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Critical limitations in elements if much alternative energy scaled up



Environmental consequences to alternative energy

Open-pit mine for uranium, Australia
Photo: Energy Resources of Australia/SkyScans

Open-pit mine for zinc and indium: Red Dog Mine, Canada
Photo: Brodie Lee

Lithium mine, Atacama desert, Chile. (Biggest deposits in Bolivia)
Photo: Robin Hammond

Potential extra topics

1. *Alternative sources for liquid fuels*
2. *Energy return on energy investment*
3. *Energy storage mechanisms*
4. *Solar photovoltaic physics*
5. *Fuel cells*