GEOS 24705 / ENST 24705
Fossil fuels III
Fossil fuels – buy organic matter and expose to high T, P

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**

```
H H H H H H H H H H
H H H H H H H H H H
C-C-C-C-C-C-C-C-C-H
H H H H H H H H H H
```

**Unsaturated**

```
H H H H H H H H H H
H H H H H H H H H H
C-C-C-C-C-C-C=CH-CH-H
H H H H H H H H H H
```

“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

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

**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 SO₂, which then makes sulfuric acid (H₂SO₄) 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 $S:C \sim .004-.02:1$)

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:

\[
\begin{align*}
\text{CH}_4 + 2 \cdot \text{O}_2 & \rightarrow \text{CO}_2 + 2 \cdot \text{H}_2\text{O} \\
4 \text{ C-H bonds} & \quad 2 \text{ C=O bonds} \\
\text{and 2 O=O bonds} & \quad \text{and 4 O-H bonds}
\end{align*}
\]
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

and the engineer George Stephenson

who bitterly accused each other of IP theft

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
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?

2004 map: more than 60% of reserves in Middle East

Where is oil found?

**Oil: what's left?**

Proven reserves in billions of barrels

- **Top 20 countries (In 2006)**
  - **World Oil**
    - **Rest of World**: 68.1
    - **Top 20 countries**: 1224.5

- **Countries and Reserves**
  - **Canada**: 178.8
  - **US**: 21.4
  - **Mexico**: 12.9
  - **Venezuela**: 79.7
  - **Brazil**: 11.2
  - **Norway**: 7.7
  - **Libya**: 39.1
  - **Azerbaijan**: 9
  - **Kazakhstan**: 7
  - **India**: 5.8
  - **UAE**: 97.8
  - **China**: 18.3
  - **Iraq**: 115
  - **Iran**: 132.5
  - **Saudi Arabia**: 264.3

Source: Oil & Gas Journal
Alberta oil sands

Localized deposit (but 140,000 km²)

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

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

Sucker rod pump:
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 CO₂ 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.

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
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

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 liquefies. (“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.

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

Is there gas production in N. Dakota?

Unlike wind, gas has a good transportation network.

Legend
- Interstate Pipelines
- Intrastate Pipelines

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

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

U.S. dry gas trillion cubic feet per year

<table>
<thead>
<tr>
<th>Year</th>
<th>History</th>
<th>2009</th>
<th>Projections</th>
</tr>
</thead>
<tbody>
<tr>
<td>1990</td>
<td>11%</td>
<td>14%</td>
<td>11%</td>
</tr>
<tr>
<td>1995</td>
<td>14%</td>
<td>20%</td>
<td>22%</td>
</tr>
<tr>
<td>2000</td>
<td>20%</td>
<td>28%</td>
<td>45%</td>
</tr>
<tr>
<td>2005</td>
<td>28%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010</td>
<td>11%</td>
<td>14%</td>
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</tr>
<tr>
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<td>45%</td>
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Note that imports projected to drop even as demand grows

Source: EIA, Annual Energy Outlook 2011

Richard Newell, December 16, 2010
Fracking (hydraulic fracturing) for shale oil and gas
Allows extraction of oil and gas from rock where it wouldn’t otherwise flow

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
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

World’s Liquid Fuels Supply

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

PENNSYLVANIA OIL PRODUCTION: 1859-1995

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.

Decreasing production and increasing consumption mean U.S. now dependent on imported oil

U.S. currently uses 25% of world production, extracts 3%

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)

<table>
<thead>
<tr>
<th>Consumption</th>
<th>Fuel Type</th>
<th>Reserve Size</th>
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<tr>
<td>33 bboe/yr</td>
<td>World coal</td>
<td>4,500</td>
</tr>
<tr>
<td></td>
<td>U.S. coal</td>
<td>1,100</td>
</tr>
<tr>
<td>30 bboe/yr</td>
<td>World oil (conventional)</td>
<td>1,200</td>
</tr>
<tr>
<td>19 bboe/yr</td>
<td>World gas (conventional)</td>
<td>1,000</td>
</tr>
</tbody>
</table>

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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</tr>
<tr>
<td>World oil (w/ oil sands)</td>
<td>1,400</td>
</tr>
<tr>
<td>World gas (conventional)</td>
<td>1,000</td>
</tr>
</tbody>
</table>

Consumption:

- **World coal**: 33 bboe/yr
- **U.S. coal**: 30 bboe/yr
- **World oil (conventional)**: 19 bboe/yr

**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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</tr>
</tbody>
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Growth in energy use is ~ 2% / yr

1 barrel of oil equivalent = 6.1 GJ

Data source: EIA

Most of oil shale - 1400 bboe – is in Green River Shale
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 \( \sim 10^{18} \) J / yr \( \sim 30 \) GW

Estimated Future U.S. Energy Requirements \( \approx 96.8 \) Quads

- Hydro: 0.94
- Bio/Geo: 3.81
- Wind: 0.06
- Solar: 0
- Nuclear: 7.48

- Coal: 20.83
- Gas: 24.73
- Oil: 38.96

Useful Energy: 44.76

- Residential: 11.89
- Commercial: 8.96
- Industrial: 26.36

- Automotive: 16.18
- Freight: 9.19
- Airlines: 2.9

Rejected Energy: 52.06
U.S. energy use, 2005

from LLNL, in quads/yr: 1 Q/yr \sim 10^{18} J/yr \sim 30 \text{ GW}
U.S. energy use, 2005 from LLNL, in quads/yr: $1 \text{ Q/yr} \sim 10^{18} \text{ J/yr} \sim 30 \text{ GW}$
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%
  
  \[
  \text{Mirrors + structure} = 50\% \text{ of cost for dish or heliostats (tower)}
  \]
  
  \[
  = 75\% \text{ of cost for trough.}
  \]
  
  *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

LEDs (light-emitting diodes)

Diodes

Photovoltaics
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!  \( W_p \neq W_{\text{actual}} \)

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/m^2
So output is ~1/5 of peak power

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

*Cry trimline 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: neodymium
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
Critical limitations in elements if much alternative energy scaled up
Environmental consequences to alternative energy

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

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

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