Society of Petroleum Engineers
Distinguished Lecturer 2010-11 Lecture Season

From Black to Gold: Nanotechnology in Upgrading of Heavy Oil

Murray R Gray
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Abstract:

Heavy oils are one of the most complex mixtures of components on earth. The largest molecules in the crude oil, in the asphaltene fraction, dominate the properties that control production, including viscosity and interfacial properties, and the options for upgrading the oil to higher API gravity. These components make upgrading of heavy oil an expensive proposition, in terms of both capital and operating expense. The key property of the asphaltenes is their tendency to associate with each other, to form aggregates a few nanometers in diameter. Research in nanotechnology is giving new insight into why the asphaltenes interact with each other, enabling new approaches to remove unwanted contaminants, to develop new catalysts, and possibly to enable synthesis of new materials derived from heavy oil. The key challenge in this area is to define the basic molecular structures in the asphaltenes, and the nature of their interactions in the oil phase and at interfaces. A wide range of new upgrading technologies have been proposed, but insight into the behavior of heavy oil at the nanometer scale allows us to analyze which of these approaches can be cheaper than current commercial technology, and which ones are unlikely to succeed.

Biography:

Dr. Murray Gray has over 20 years of research experience in upgrading of heavy oil and oil sands bitumen. He is currently Director of the Centre for Oil Sands Innovation at the University of Alberta. His success in collaborative research with industry has been recognized by numerous awards and prizes, including the Syncrude Innovation Award (1996), and the Industrial Practice Award of the Canadian Society for Chemical Engineering (2003). In 2005 he was elected a Fellow of the Canadian Academy of Engineering. In 2006 he was awarded a Canada Research Chair and an Industrial Research Chair in Oil Sands Upgrading. Gray obtained his Ph.D. in Chemical Engineering from the California Institute of Technology in 1984. He also holds a M. Eng. degree with a specialization in Petroleum Engineering from the University of Calgary (1980) and a B.Sc. in Chemical Engineering (with honours) from the University of Toronto (1978).

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From Black to Gold:
Nanotechnology in Upgrading of Heavy Asphaltic Crude Oils

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Outline

- Benefits and challenges of upgrading heavy oils
- Nanotechnology – definition and significance for the petroleum industry
- Definition of asphaltenes and their significance
- Nanoscale behavior of asphaltenes
- Molecular composition
- Upgrading of heavy oils based on nano-science

Heavy Oil

Heavy oil facility near
Bakersfield, CA
wwww.energyinsights.net

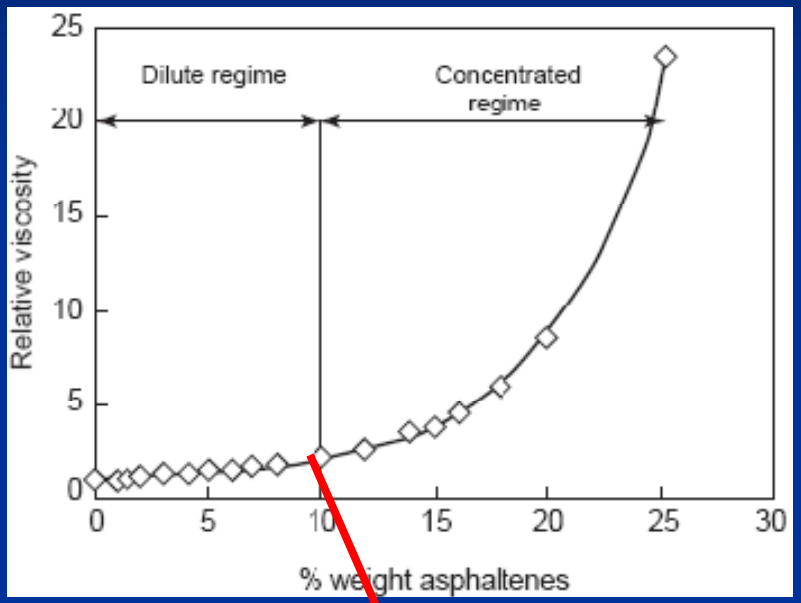
Kern River Crude – 13 API
1.1% sulfur, 56% residue

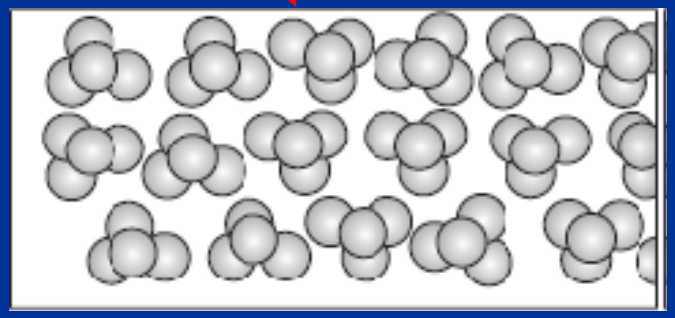
- Dense crude oil with API° < 20
- Significant resources worldwide
- Lower H, higher S, N and metals than light crudes
- High proportion of the barrel cannot be distilled, even under vacuum – up to 50% (vacuum residue)

Viscosity of Heavy Oil

- Crude oil viscosity normally increases with density
- Bitumen with 9°API, 1,000,000 cP at 15°C
- 1-methyl naphthalene: 9.8 °API, viscosity 2.6 cP
- Mercury: API°=-121 and viscosity 1.5 cP
- Why?

Why is heavy oil viscous?





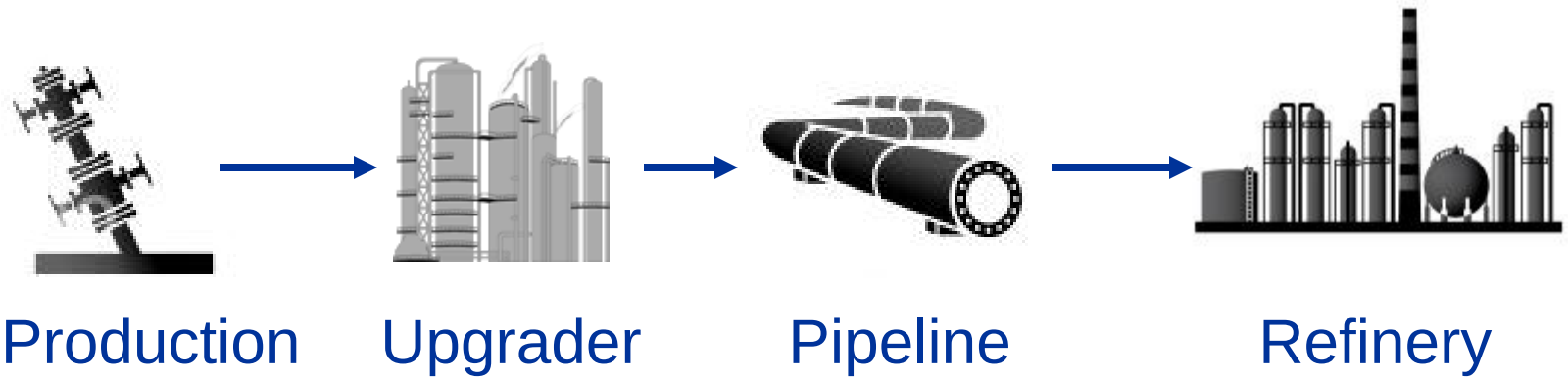
- Viscosity of liquids is due to intermolecular forces
- Larger molecules in heavy oil give more interaction
- Asphaltene fraction gives aggregates in the oil phase, size 5-20 nm
- Overlap of aggregates gives very high viscosity

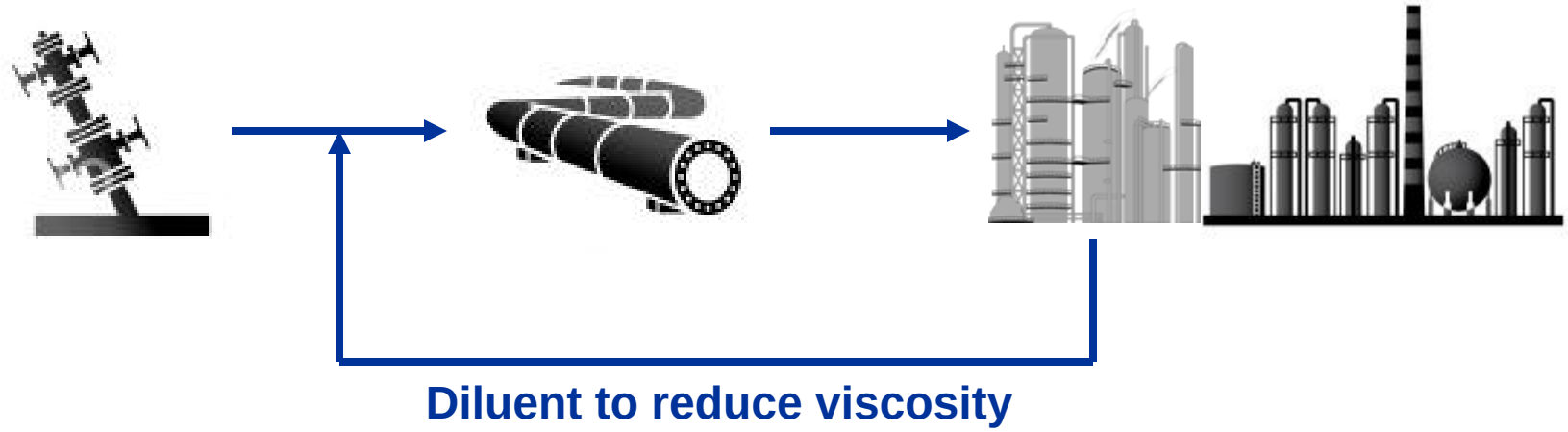
Rev. Inst. Fr. Petrole, 2004

Incentives for Upgrading of Heavy Oil

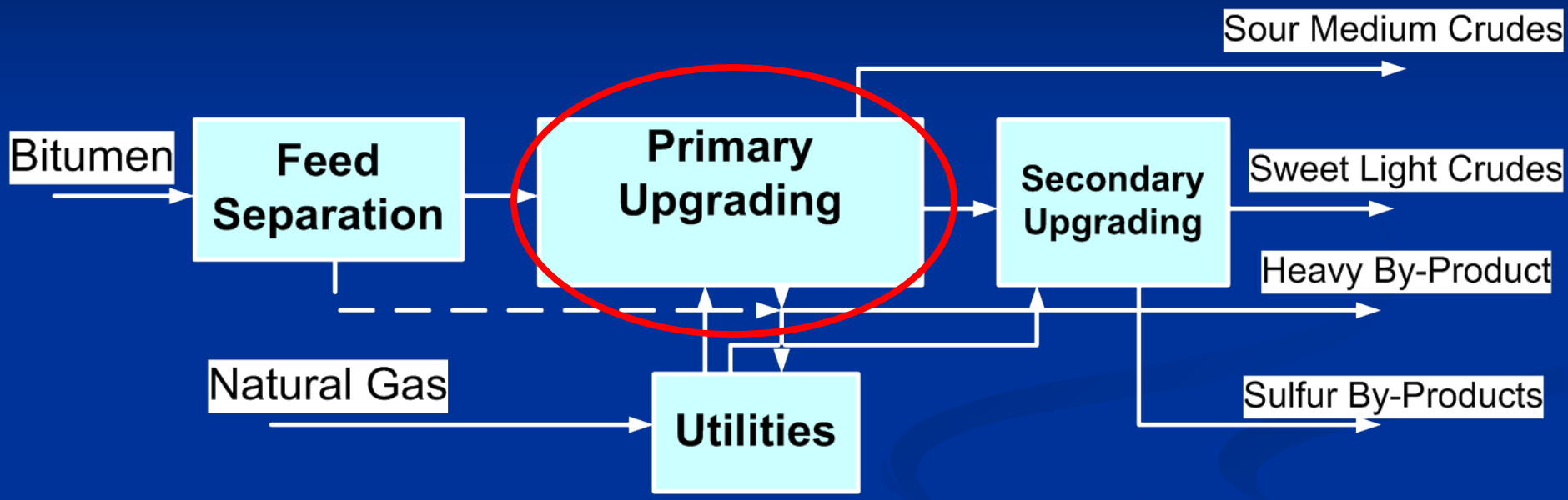
- Transportation: Reduce viscosity to enable transport without adding a solvent (Canada, Venezuela) or heating pipeline (Alaska)
- Price: Increase the API gravity, reduce sulfur content
  - Refineries value high API crude oils
  - Viscosity is not a significant issue for refineries

Example Upgrader Configurations





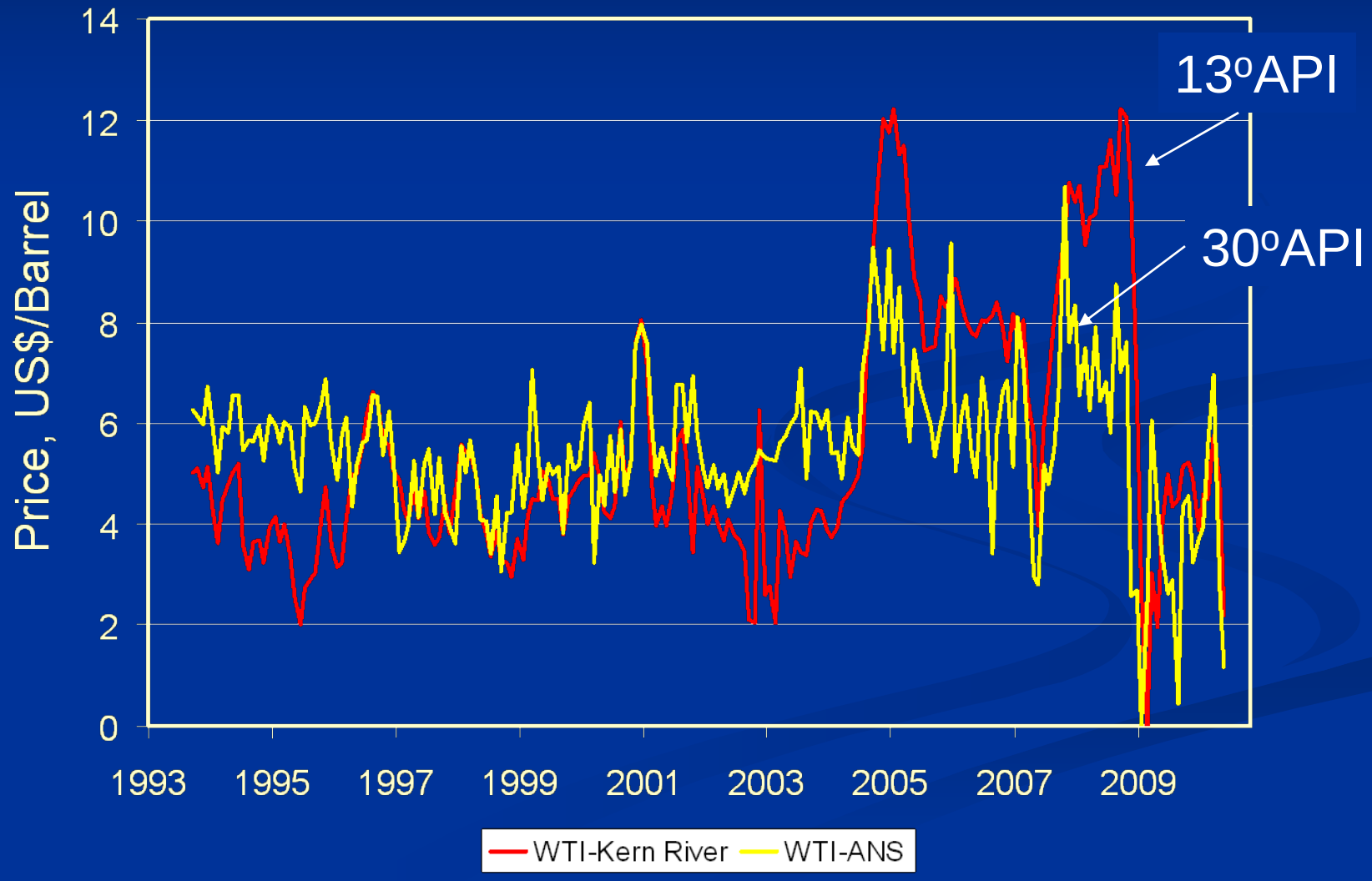
Upgrading Processes



- Capex: $30K-$100K per (barrel/day) of throughput
- Typical scale: 50-150 kBBL/D
- Operating costs $5-$10/BBL

Crude Oil Differentials

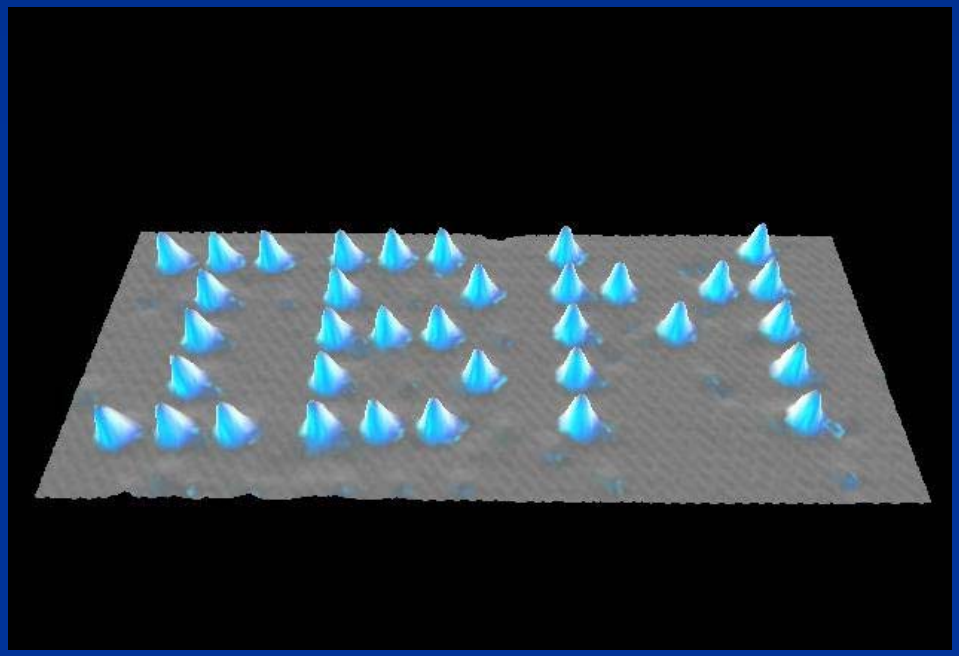
(California Kern River-WTI and ANS-WTI)



Nanotechnology

- Richard Feynman, 1959 lecture at Caltech, "There is plenty of room at the bottom"
  - Implications of constructing devices atom by atom
  - "At the atomic level, we have new kinds of forces and new kinds of possibilities, new kinds of effects. The problems of manufacture and reproduction of materials will be quite different."
- Franks, 1987: Nanotechnology is "..technology where the dimensions and tolerances in the range 0.1 – 100 nm (from the size of an atom to the wavelength of light) play a critical role"

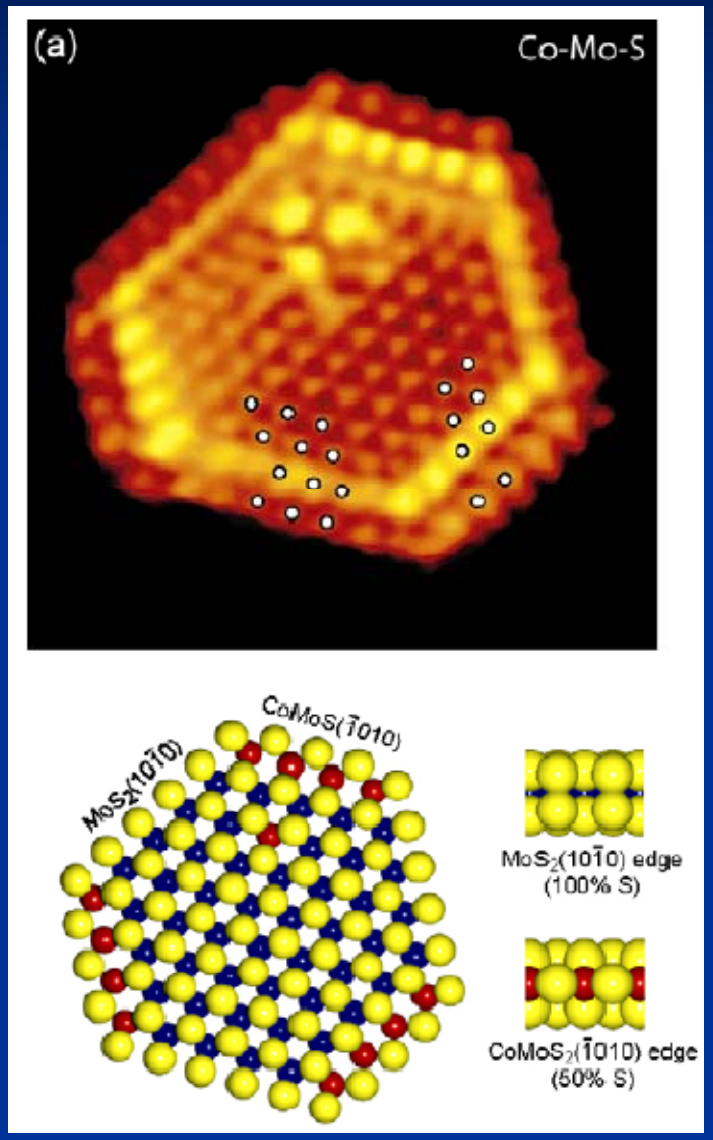
Iconic Image of Nanotechnology



STM image of xenon atoms on Ni, Don Eigler, 28 Sep 2009

- Franks (1987) defined areas:
  - Ultrafine powders of nanoscale particles
  - Precision machining and materials processing (tolerances in the nano range)
- Applications:
  - Nanoelectronics – "molecular electronics", including both semiconductor, organic and hybrid systems
  - Scanning tunneling engineering – STM not only as a probe of atomic-level structure but as a tool for fabrication atom by atom
- How does this relate to heavy oil?

Profitable Nanotechnology



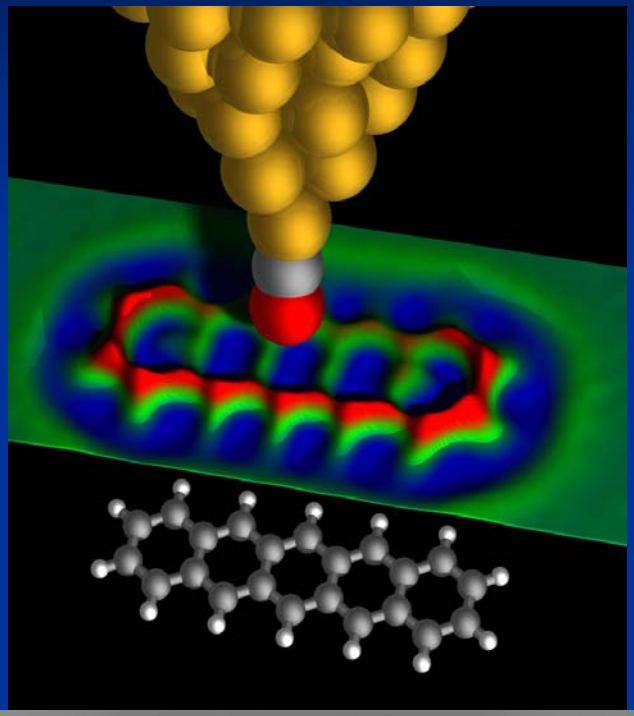
Besenbacher et al., 2008

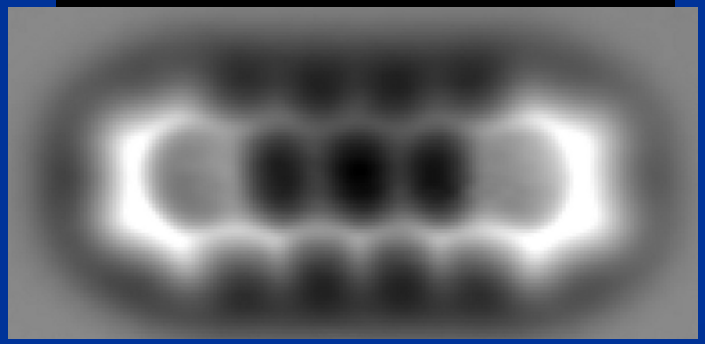
- Catalysts for making low-sulfur diesel and gasoline
- Co+Mo or Ni+Mo on alumina with high-pressure hydrogen
- First used in 1940's
- STM shows brim sites of high activity
- "BRIM" catalysts commercialized in 2004

Asphaltenes: Turning adversaries to allies

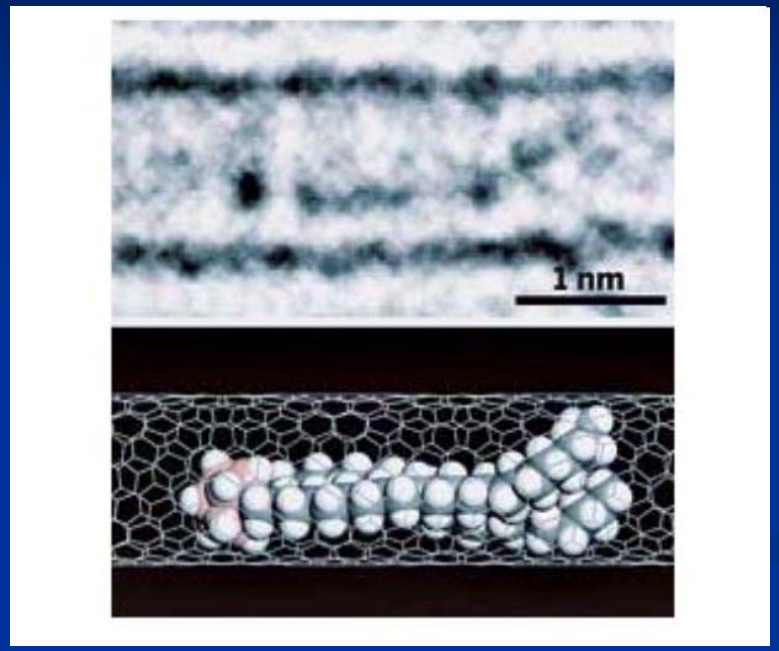
- Most difficult fraction in heavy oils
- Soluble in toluene, and insoluble in n-heptane
- Understanding asphaltenes unlocks the value of bitumen/heavy oil resources (*i.e.* upgrading)
- Nanotechnology is the key
  - Understand, measure, and control behavior at length scale < 0.1 μm

Imaging of Individual Molecules





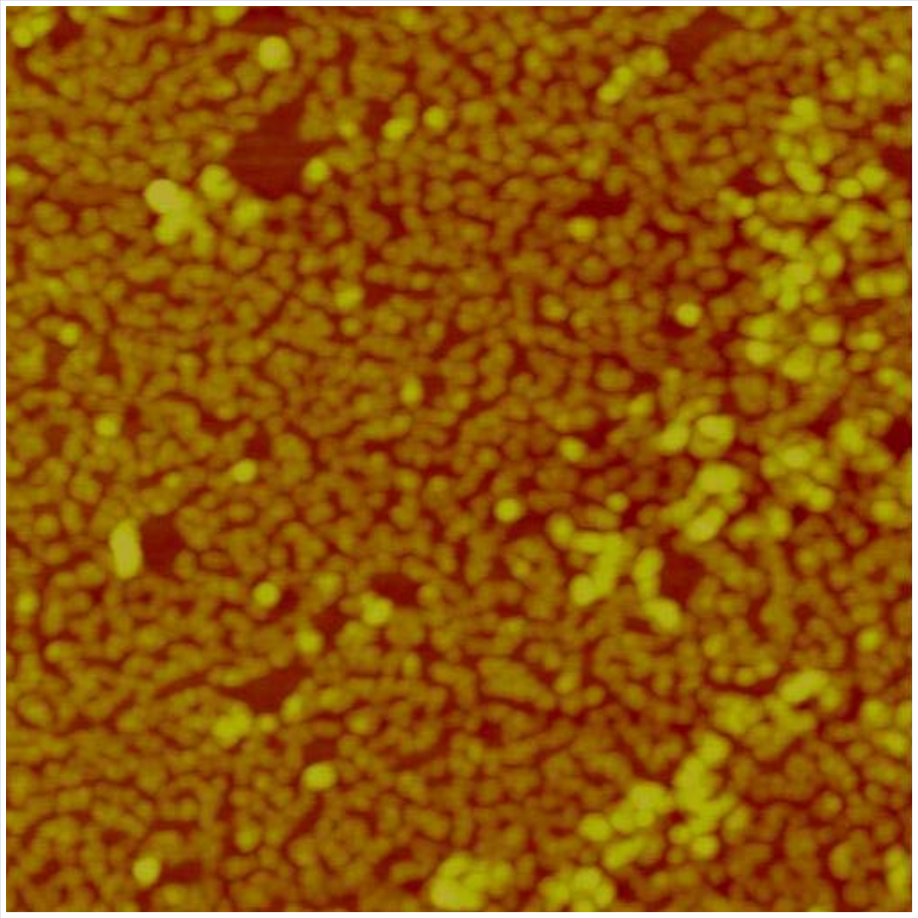
Gross et al., Science, 2009



Nakamura et al, Science, 2007

- STM - Attach CO molecule to tip of probe
- TEM – Isolate molecule in a carbon nanotube

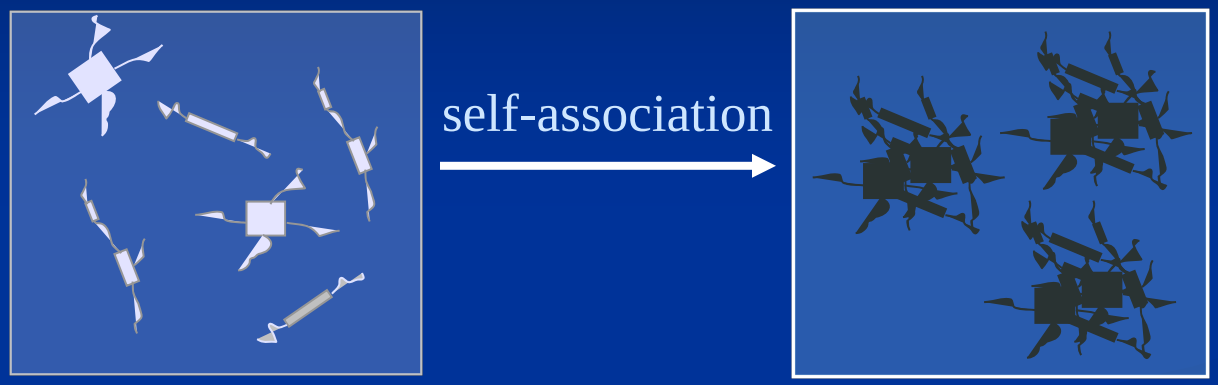
Image of Nano-Aggregates of Asphaltenes



1 μm

30 minute immersion of silicon wafer in dilute solution of asphaltene in toluene
Atomic force microscopy images courtesy JH Masliyah and Z Xu

Asphaltenes in Heavy Oil



molecules

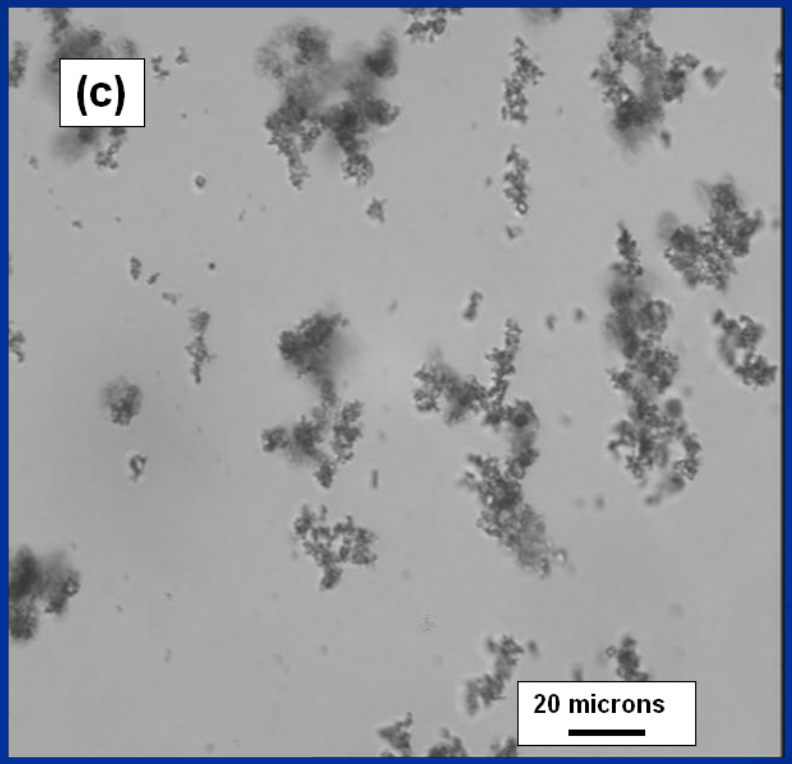
Aggregates (5-10 nm)

Self-association results in:

- increased potential to precipitate or form a dense phase
- increased viscosity
- change in interfacial behavior

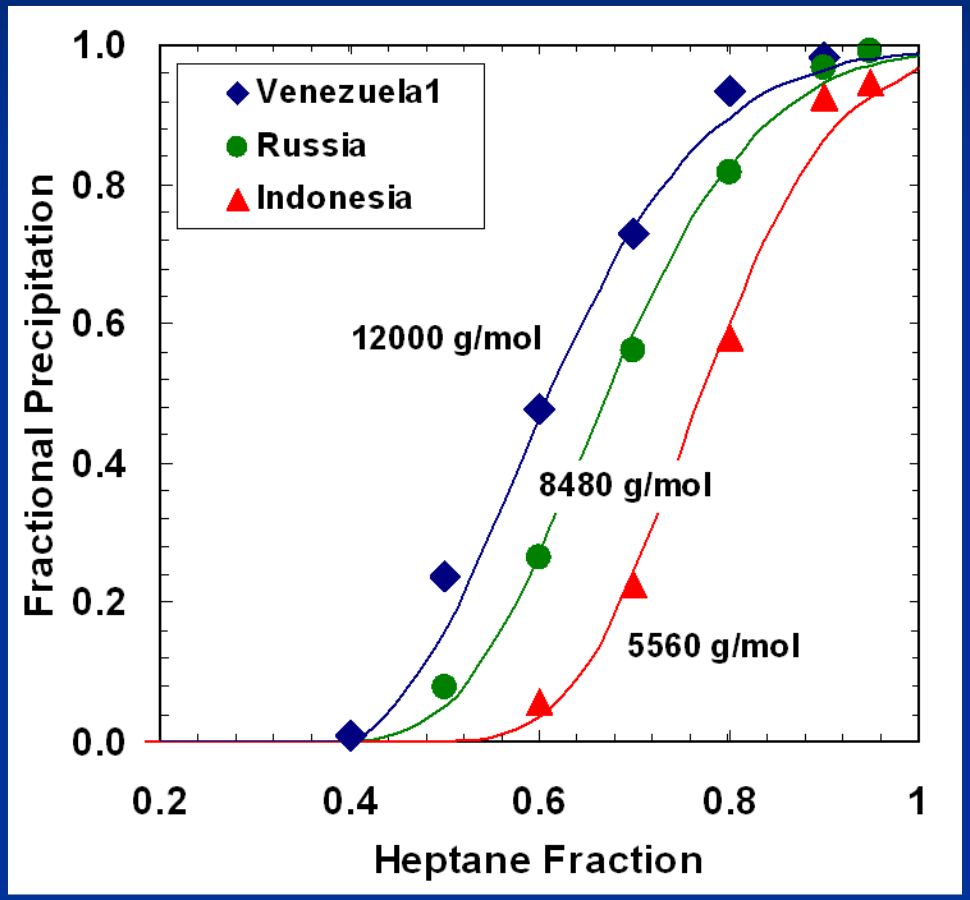
Must be accounted for in models of **phase behavior** and physical properties

Asphaltene Precipitation



(1 - 100 μm scale)

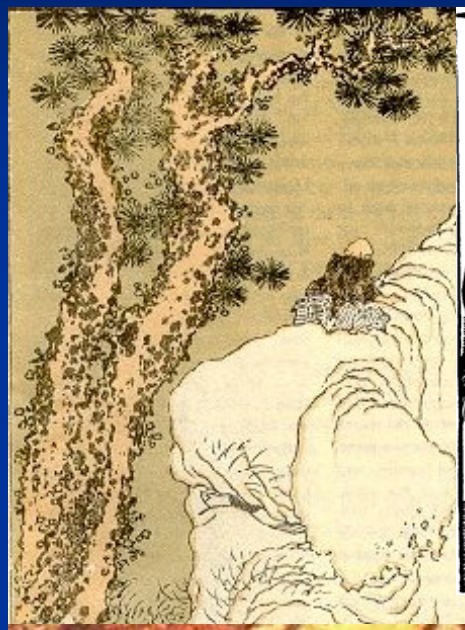
Precipitation in Solvents
Regular Solution Model

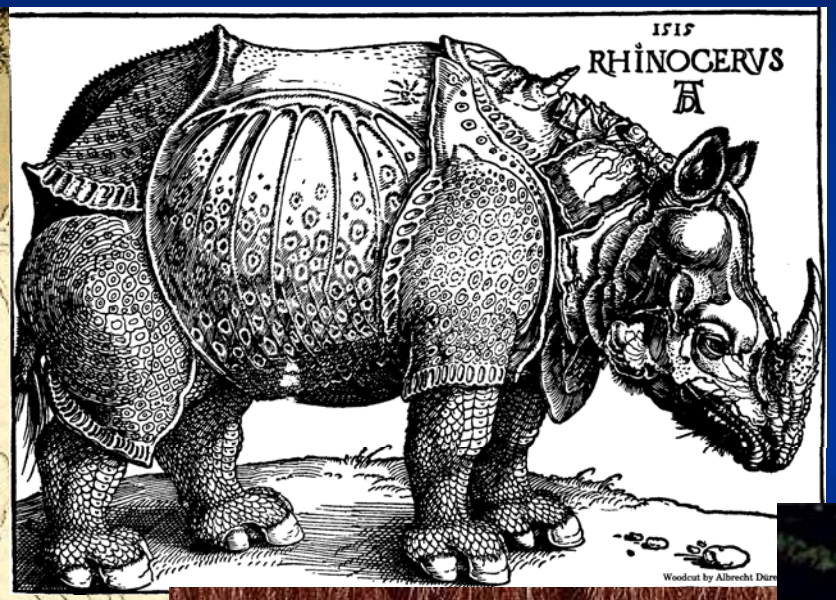


- Asphaltene yields are predictable when based on the average molar mass of the nano-aggregates

H Yarranton, University of Calgary

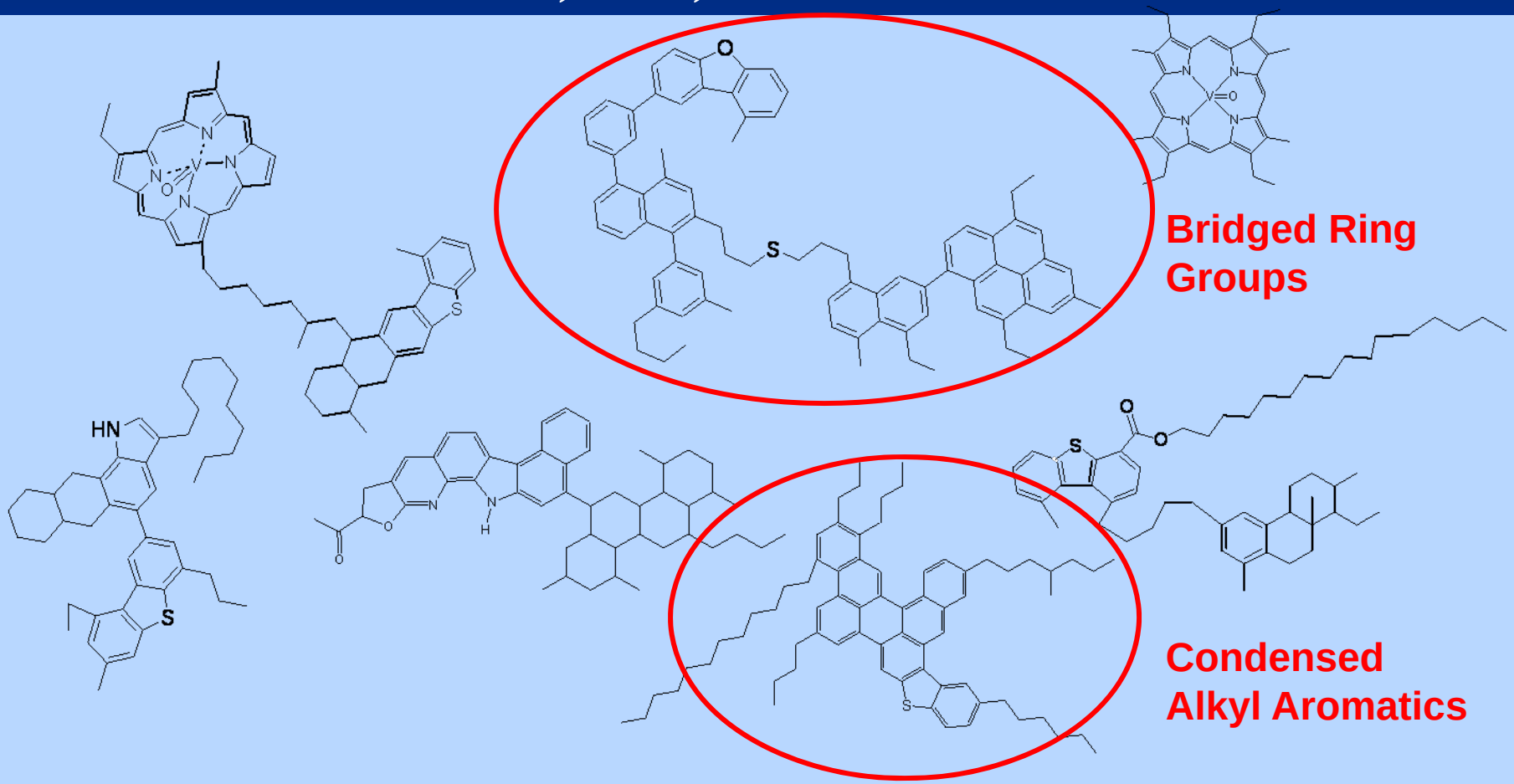
What do asphaltenes look like?



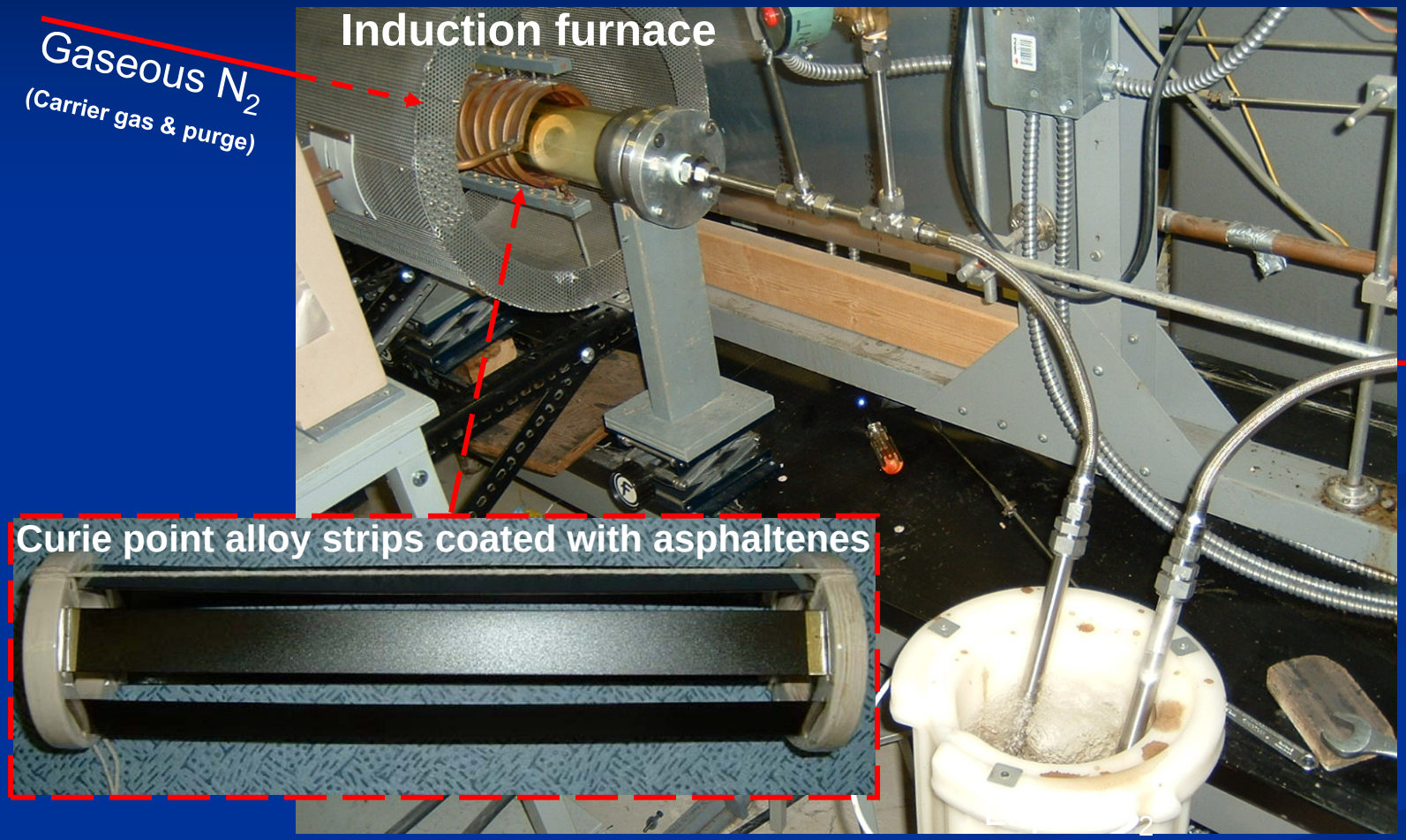


How are asphaltene molecules constructed?

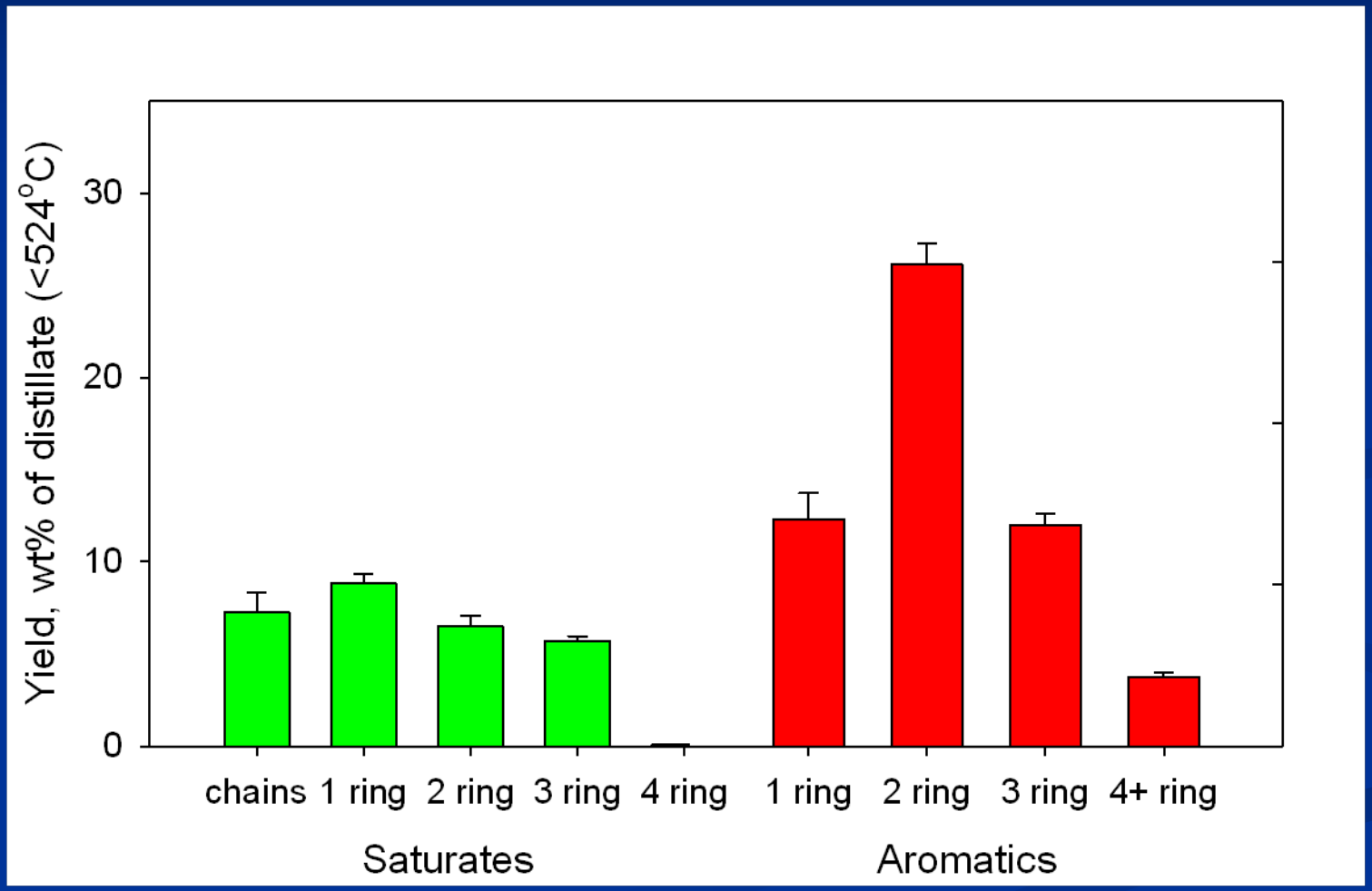
Based on Sheremata et al., 2004; Strausz 1999



Pyrolysis apparatus



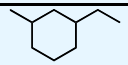
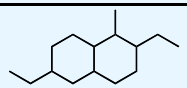
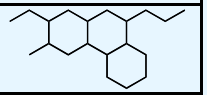
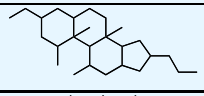
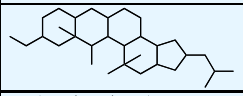
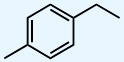
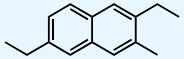
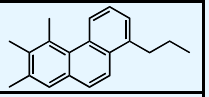
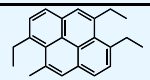
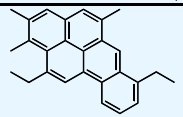
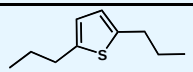
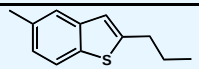
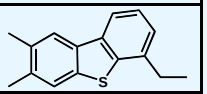
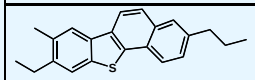
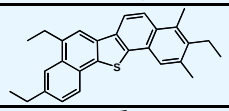
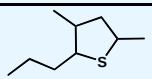
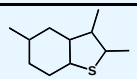
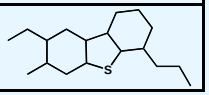
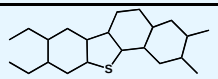
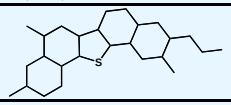
Classes of products:
Gas chromatography-mass spectrometry

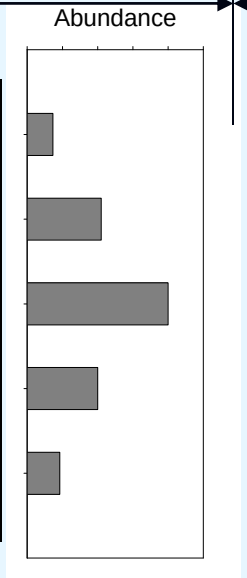


(1 ring includes olefins)

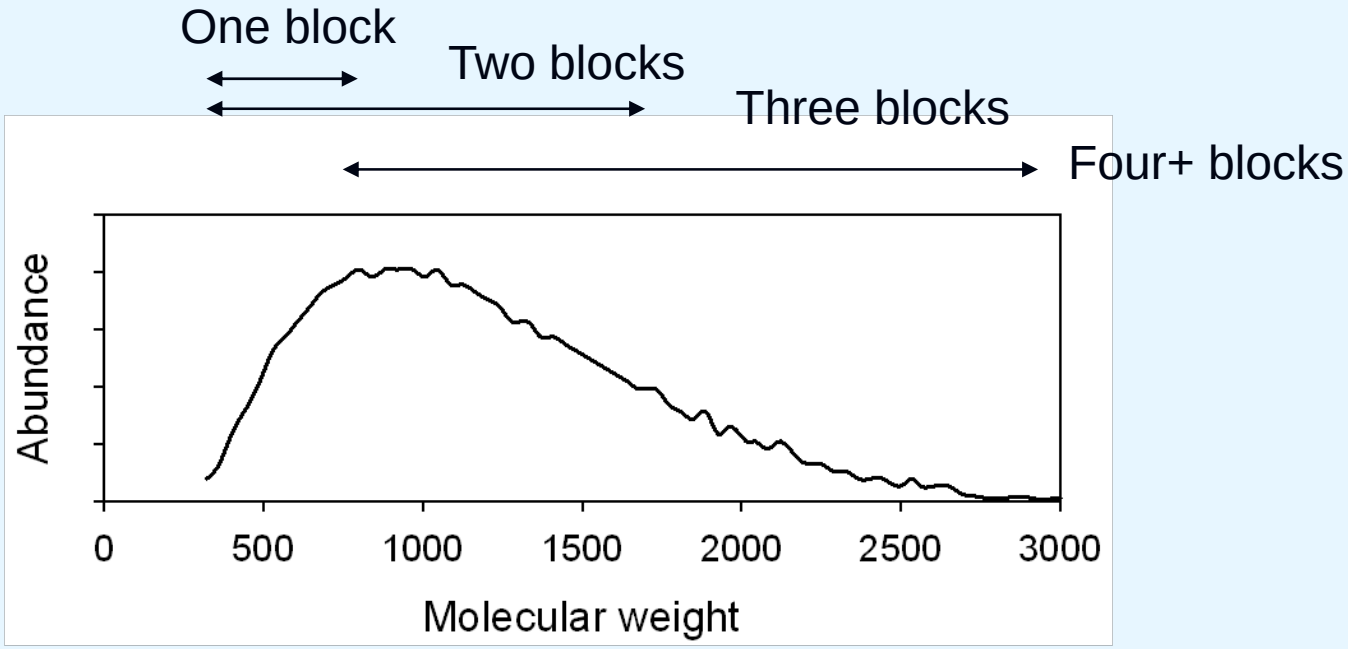
Small Blocks
Boiling < 538°C

Large Blocks
Boiling > 538°C

# Rings	0	1	2	3	4	5	6	7
Paraffins	n-C_{12} to n-C_{30}							
Cycloalkanes								
Aromatics								
Thiophenes								
Sulfides								

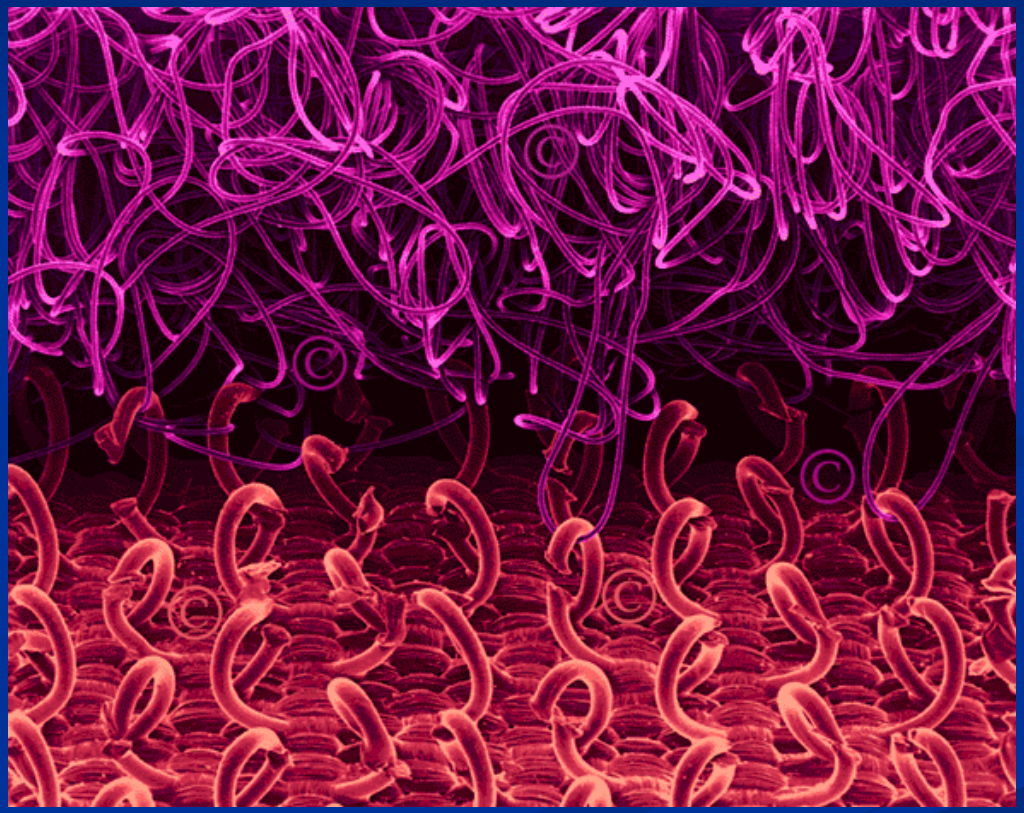


Asphaltenes built up from 1-10 large and small building blocks



Why do asphaltenes seem so complex?

- Asphaltenes = "Molecular velcro"
- Stable aggregation even in good solvents
- Much more difficult to analyze than DNA



http://www.ldeo.columbia.edu/res/fac/micro/images.section/pages/velcro.html

Nanotechnology Opportunities

- Design catalysts for large molecules in heavy oil
  - Atomic level imaging + computer simulation + controlled synthesis of catalysts
- Design dispersants to prevent aggregation of asphaltenes
  - Control molecular behavior during upgrading
  - Control viscosity?

In Situ Upgrading

- Why not upgrade *in situ* to avoid capital expense?
  - Reduce viscosity – crack large molecules
  - Reduce density – increase H content, reduce S & N
  - Significant reactions require temperatures > 480°F
- Two approaches under development:
  - Partial combustion to generate hydrogen in situ
  - Coke the oil in place

In Situ Combustion with Horizontal Wells (THAI Process)

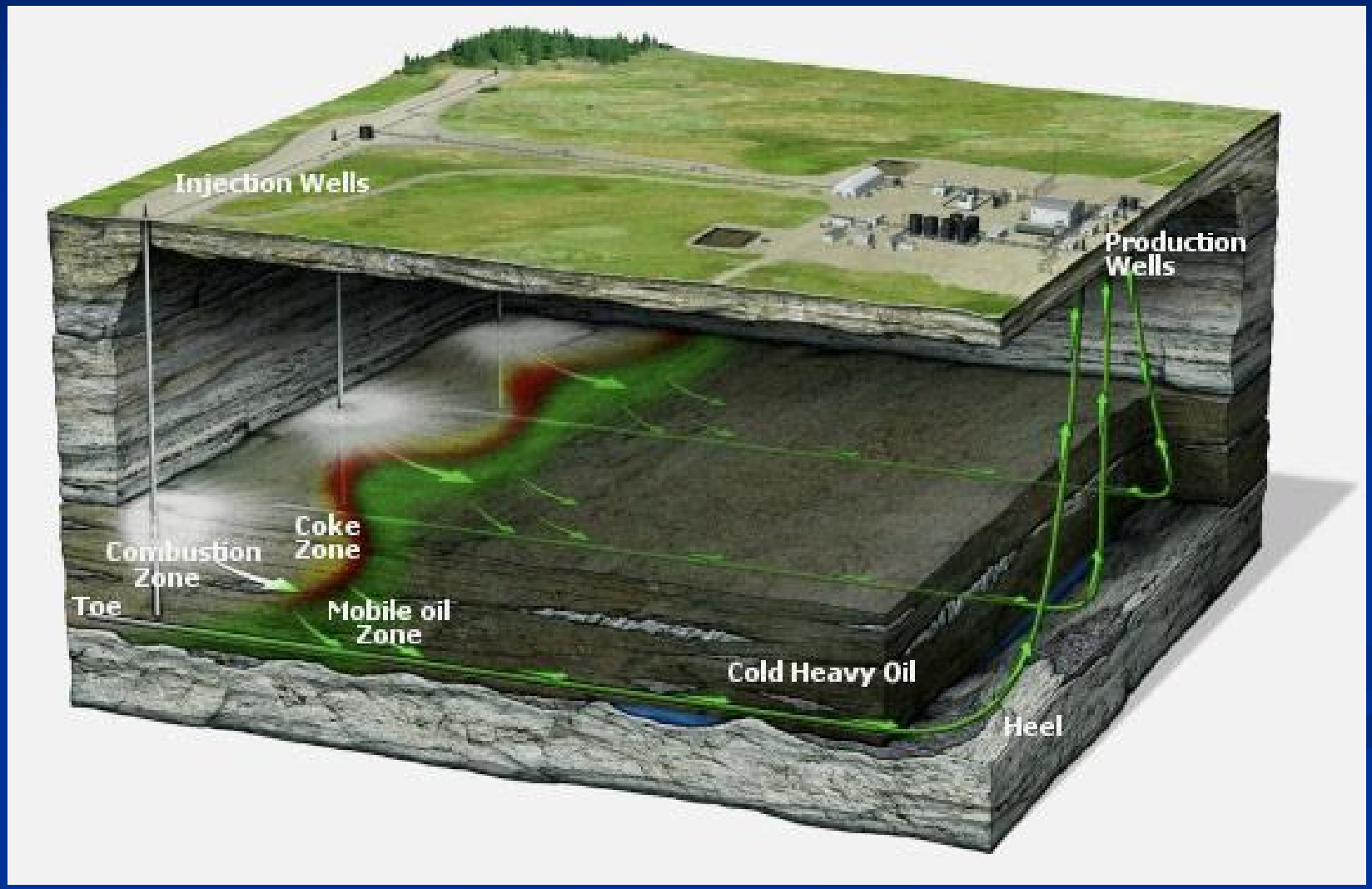
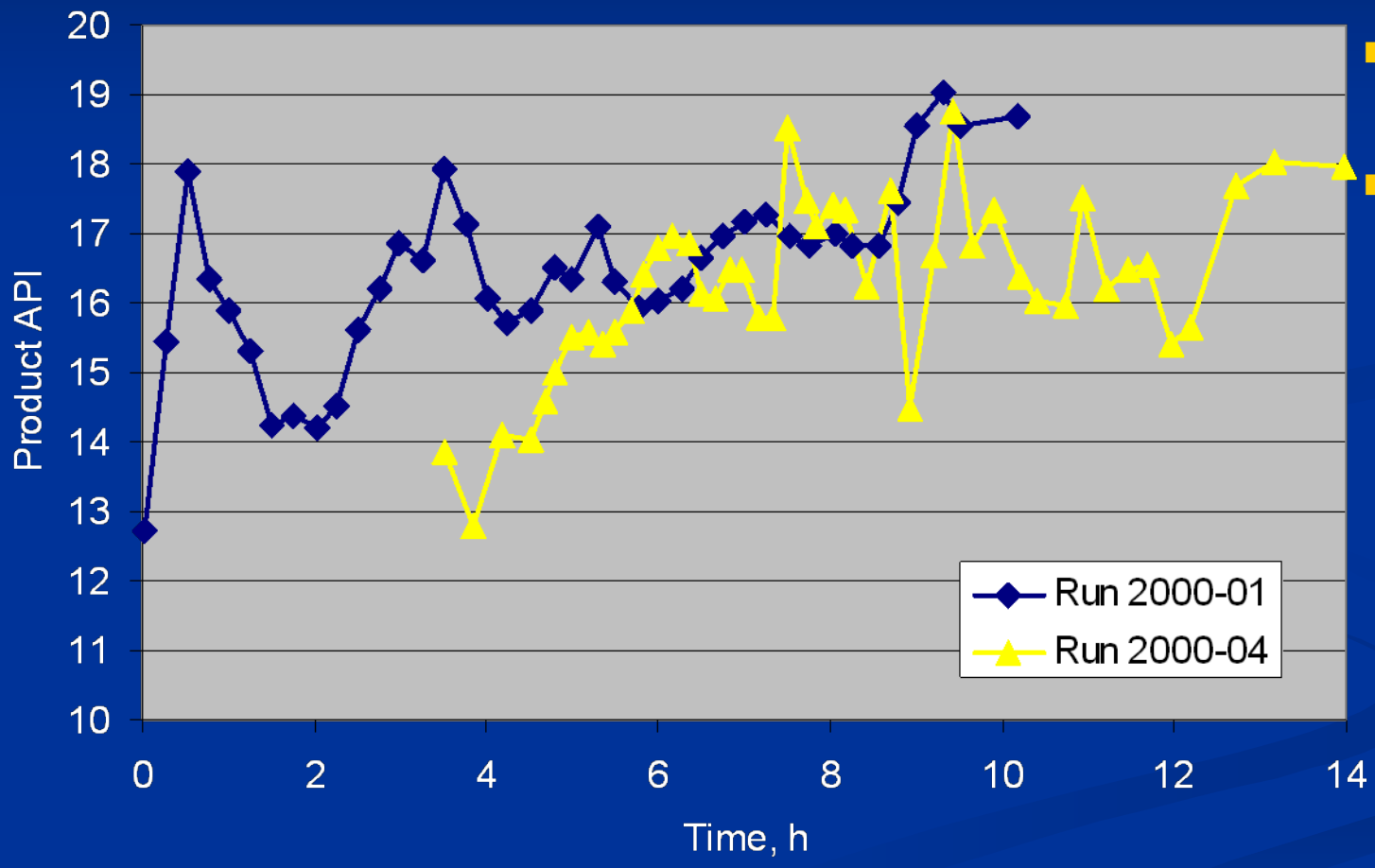


Image from Petrobank Resources

THAI product quality – Lab tests

API gravity of starting crude oil = 8



- Highly variable results
- Offers reduction in diluent

Greaves et al., Bath University

Gas composition from THAI – Laboratory tests

Overall period (h)	14.5
Pre-ignition period (h)	3.5
Dry combustion phase (h)	11
Peak temperature (°C)	600–750
Average composition of produced gases (%)	
CO_2	17.0
CO	5.6
O_2	1.38
CO/(CO2 + CO)	0.248
H/C	0.0
O_2 utilization (%)	93.4

- Control of residual oxygen is a challenge
- Can the CO be used?

In situ Combustion PLUS Catalysis

- Harness the CO from partial combustion:

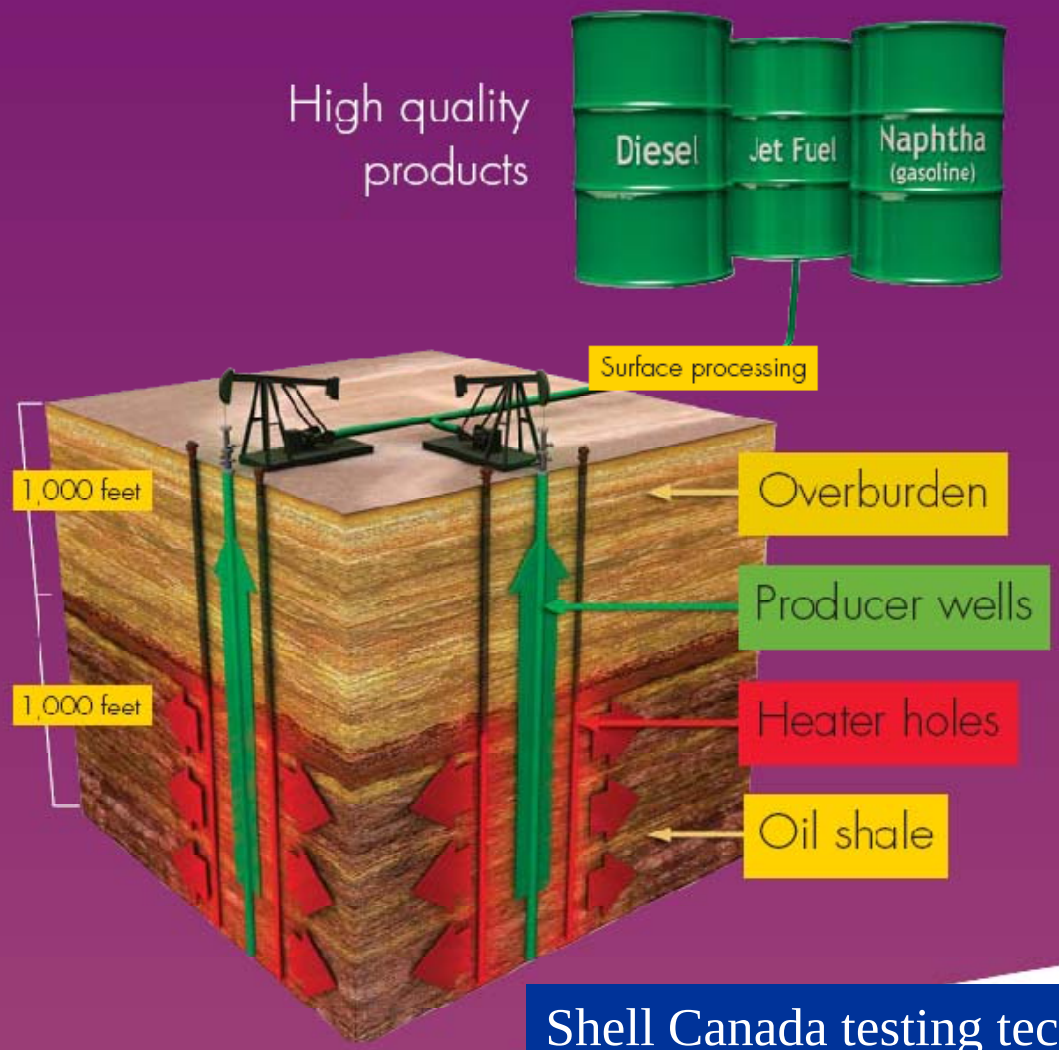
$$CO + H_2O = H_2 + CO_2$$

- Catalyst needed to combine the hydrogen with the oil
- Two approaches:
  - CAPRI - Place catalyst around production well bore to make use of gases to hydrogenate oil:
  - Inject nanoparticle catalysts (MoS_2 based into the well)
- Catalysts require high temperature (>300°C), high pH_2, long time (1 h)

Prospects for Combustion-Based *In Situ* Upgrading Processes

- Advantages:
  - cheapest possible fuel for thermal production
  - Improved stability in comparison to fireflooding
- Disadvantages:
  - Complex transport processes sensitive to reservoir heterogeneities
  - Oxygen breakthrough and oxidized product
  - Tradeoff between heat to mobilize oil versus upgrading
  - Cost, activity and recovery of catalysts?
- Better prospects for production than for upgrading

Shell In Situ Technology for Oil Shale (Mahogany Project)



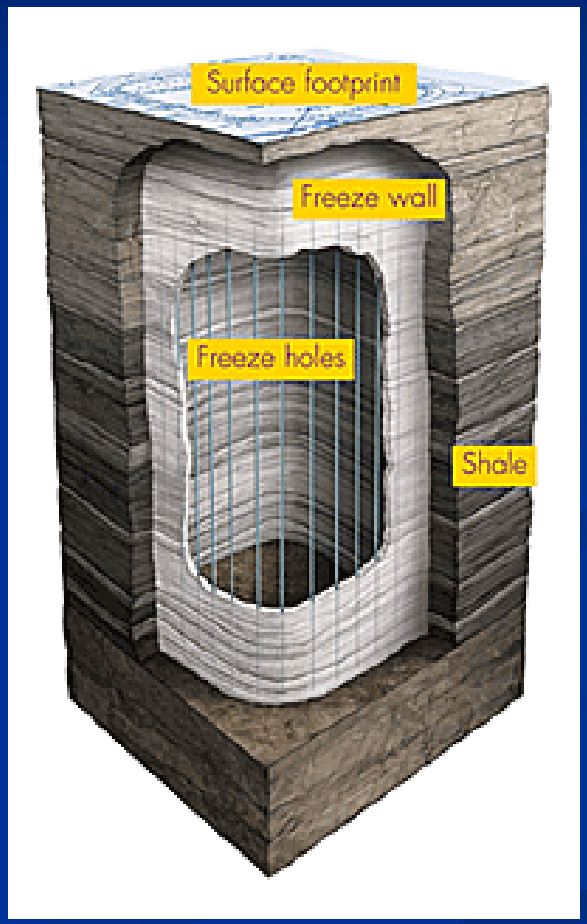
Innovative technology

- Electric heaters gradually heat shale beneath surface
- Rock formation heated slowly over time to 650 to 750° F
- Heat converts kerogen in oil shale into oil and gas
- Target depth zone typically 1,000 to 2,000 feet
- Products are brought to surface using traditional methods
- Produces approximately 1/3 gas and 2/3 light oil
- Requires fewer processing steps to produce high quality transportation fuels such as diesel, jet fuel and naphtha (gasoline)

Shell Canada testing technique at Peace River

Freeze Wall Technology

- Slow heating of rock to high temperature
- Aquifers bring active water flow
- Need to control fluid flows in subsurface
- Freeze the fluids, then heat inside the wall



Prospects for *In Situ* Coking Process

- Pilot testing in Peace River on bitumen
- Benefits:
  - Scalability in heterogeneous reservoirs and carbonates
  - No air introduced
  - Significant upgrading to >30°API
  - Carbon free production with electric heaters
- Disadvantages
  - High energy input; simulations suggest 8:1 output/input ratio
  - Mobile liquids (water and bitumen) must be controlled
  - Olefins may affect transportation

Conclusions

- Heavy oils are complex nanofluids
  - Chemically complex asphaltenes
  - Nano-aggregation behavior of asphaltenes dominates phase behavior and processing
- Example of catalysts for sulfur removal suggests a path forward
  - Combine modern tools for imaging and computation
  - Control nanoscale behavior
- Upgrading of heavy oils is advancing based on nano-science

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