Unconventional Crude Oils Briefing

August 13, 2014

CDR Gregory Hall, Ph.D.

Acknowledgments

- RDML Brown, CG-5R
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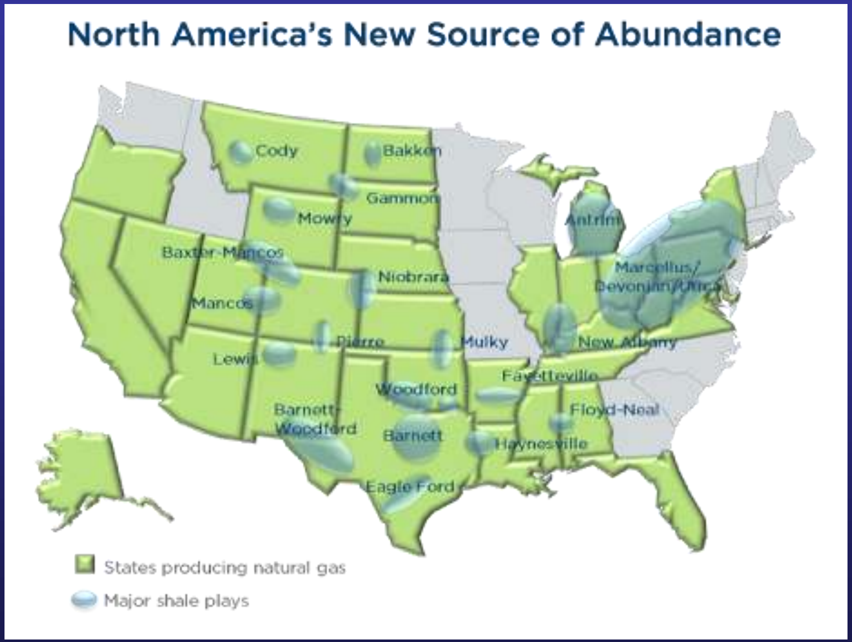
Unconventional Crude Oils

- Issue Statement
  - New production in North America
- Crude oil Composition and Properties
  - What is crude oil?
  - How do we measure/characterize?
  - Specifics for Light Crude Oils & Dilbit
- CG Implications
  - Facilitated discussion / Q&A

Issue – Part A

"In 2012, America's total oil production averaged 6.5 million barrels a day, according to government estimates. This year, U.S. oil production is expected to set new records, rising over 30 percent to 8.53 million barrels per day."

"Since 2007, U.S. crude reserves have risen by over 40% and are now at a 36 year high."



America's Energy Revolution , API, 2014

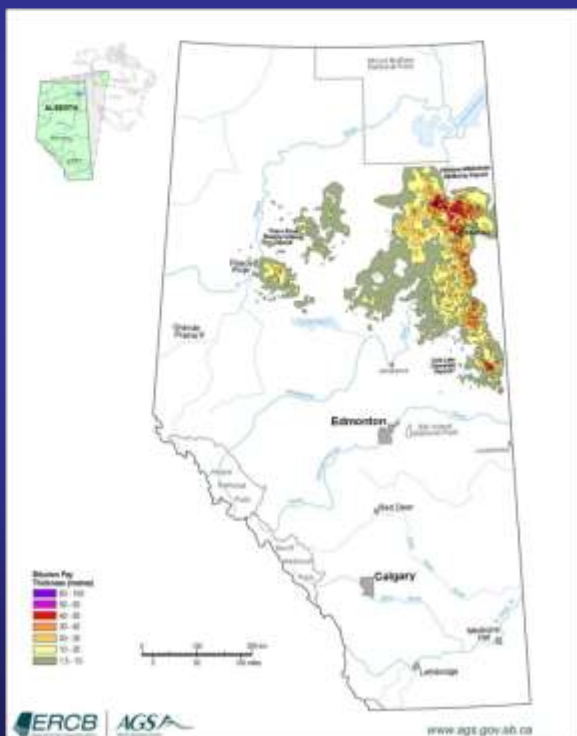
Issue – Part A

Derailment & explosion – Lac Mégantic

Paul Chiasson/CP

Issue – Part B

"The Canadian oil sands contain the world's third-largest oil reserves after Saudi Arabia and Venezuela…. Increased exports of oil sands products have been proposed by industry, involving pipeline, rail and marine tanker transport. "



Canadian Crude Oil Production (million b/d)					
	2013	2015	2020	2025	2030
Western Canada	3.2	3.7	4.6	5.6	6.4
Conventional	1.3	1.4	1.5	1.5	1.5
Oil Sands	1.9	2.3	3.2	4.1	4.8
Eastern Canada	0.2	0.2	0.3	0.2	0.1
Total *	3.5	3.9	4.9	5.7	6.4

*Totals may not add due to rounding

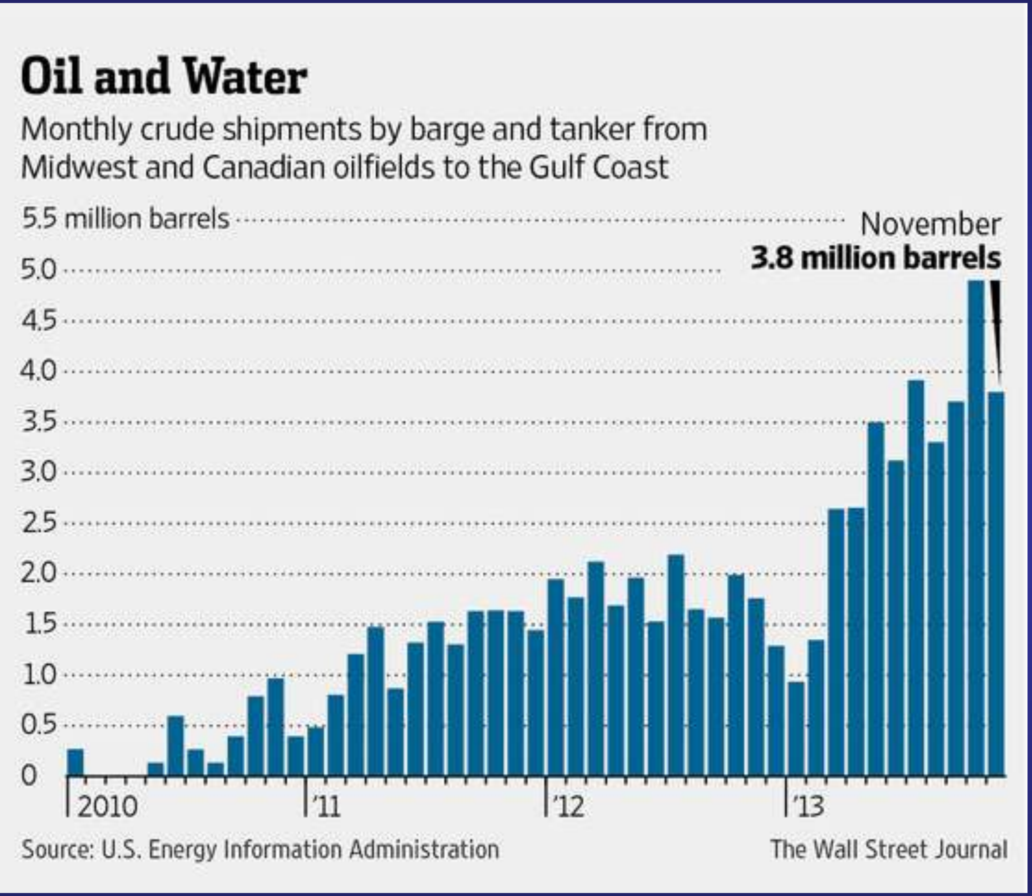
Federal Government Technical Report -Properties, Composition and Marine Spill Behaviour, Fate and Transport of Two Diluted Bitumen Products from the Canadian Oil Sands , Environment Canada Emergencies Science and Technology. 2013

Issue – Part B

Enbridge Pipeline Spill

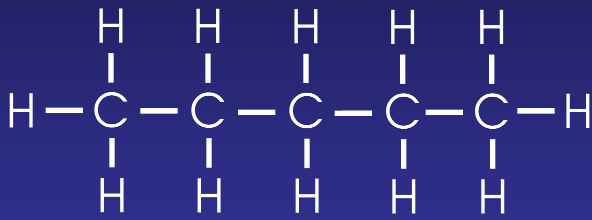
http://www.epa.gov/enbridgespill

Issue

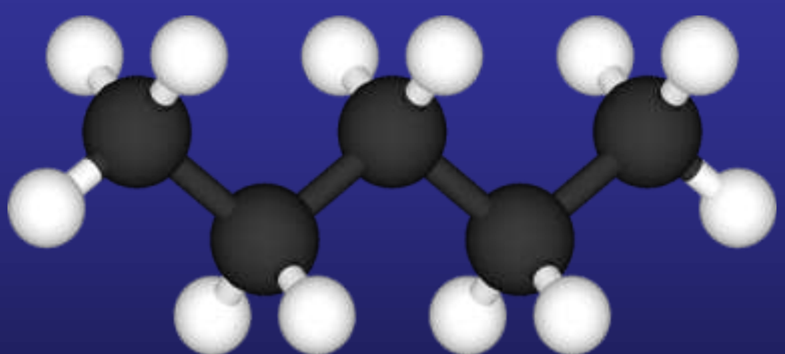

Oil and Water
Monthly crude shipments by barge and tanker from Midwest and Canadian oilfields to the Gulf Coast
5.5 million barrels
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
2010
'11
'12
'13
November
3.8 million barrels
Source: U.S. Energy Information Administration
The Wall Street Journal

Crude Composition

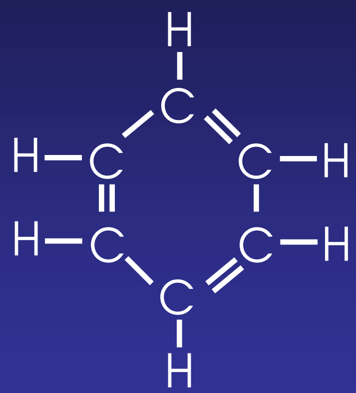
Organic Chemistry Review “HCs”



alkane



Organic Chemistry Review "HCs"



aromatic

Petroleum – The Molecules

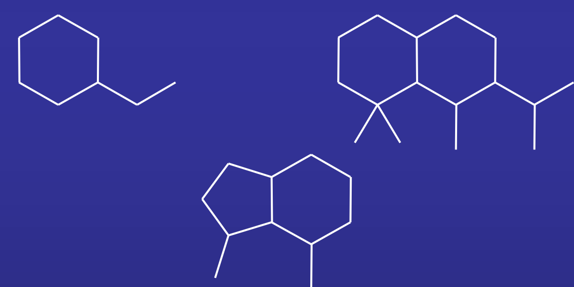
alkanes (15-20%)

“C8”

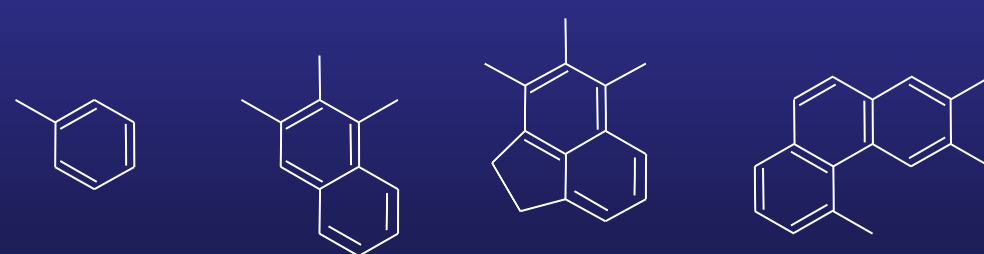
branched alkanes (15-20%)

paraffins

cycloalkanes (30-40%)



aromatics (20-45%)



Petroleum – The Molecules

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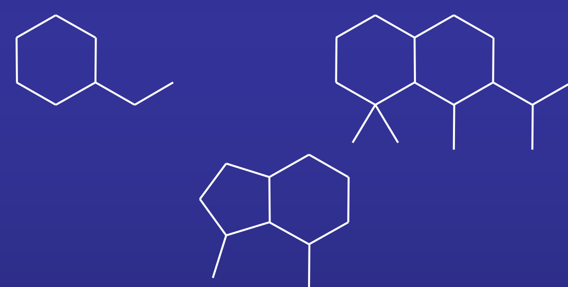
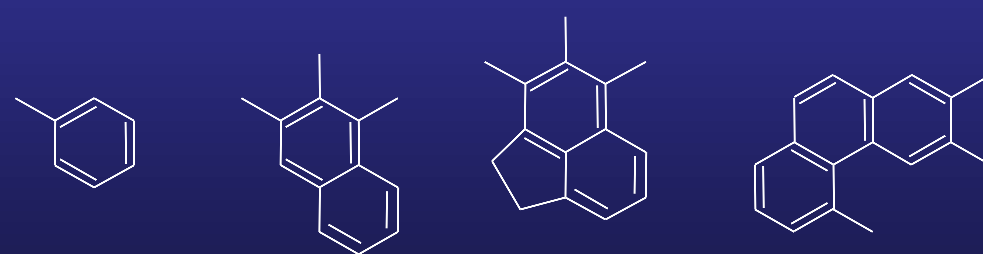


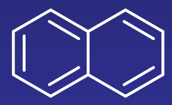
aromatics (10-45%)

Bakken (9.3%)
Dilbit (5 -11%)

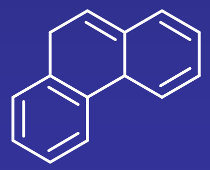


At least 1 report for Bakken that the aromatic fraction is a little high in small PAH

Aromatics – PAH
Polycyclic Aromatic Hydrocarbons



Naphthalene

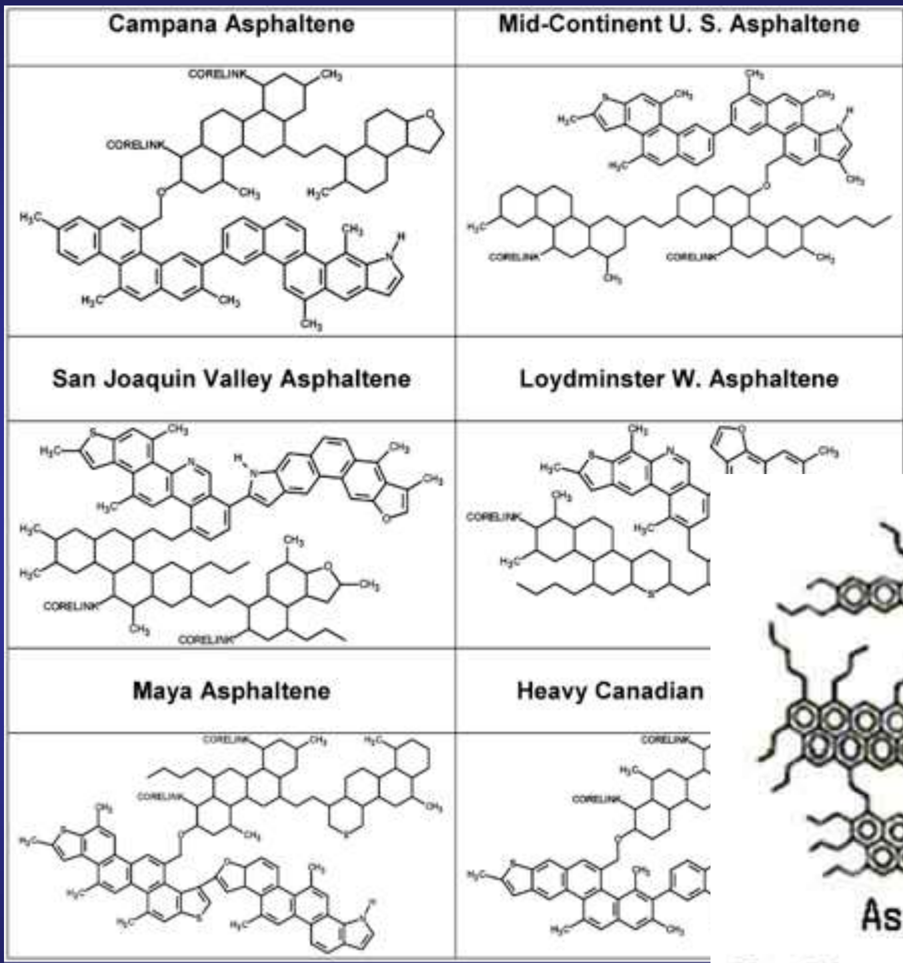


Phenanthrene

Pyrene

Benzo[a]pyrene

Asphaltenes & Resins



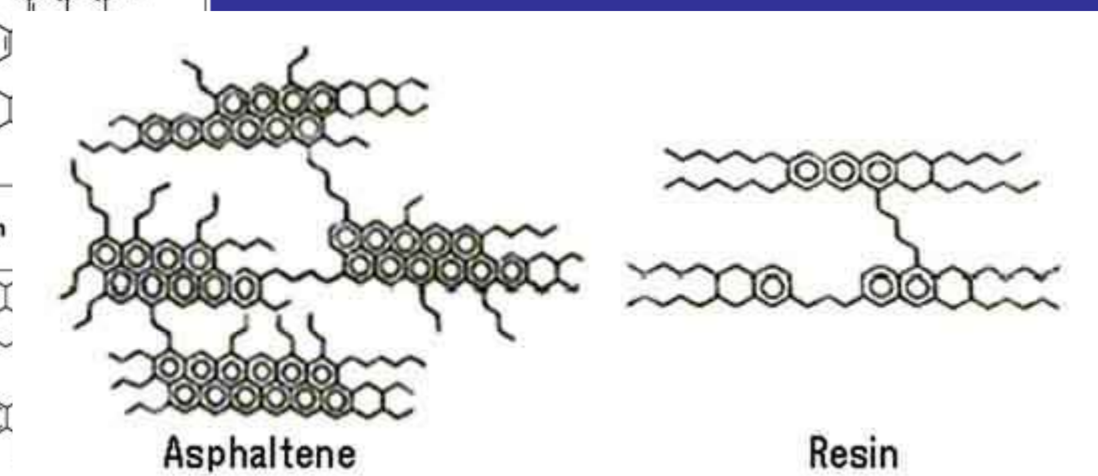


Fig. 16
Structures of asphaltene and resin from Khafji crude oil

Petroleum – Isomers

Pentane
Hexane
Heptane
Octane-decane
Undecane-Pentadecane
Hexadecane and higher

2-Methylpentane
3-Methylpentane
2-Methylhexane
3-Methylhexane
2-Methylheptane
3-Methylheptane
2-Methyloctane
3-Methyloctane
2-Methylnonane
3-Methylnonane
4-Methylnonane
Pristane (isoprenoid)

Cyclopentane
Methylcyclopentane
Cyclohexane
Ethylcyclopentane
Methylcyclohexane
1,1-Dimethylcyclopentane
1-*trans*-2-Dimethylcyclopentane
1-*cis*-3-Dimethylcyclopentane
1-*trans*-3-Dimethylcyclopentane
Propylcyclopentane
Ethylcyclohexane
1-*trans*-2-Dimethylcyclohexane
1-*cis*-3-Dimethylcyclohexane
1,1,3-Trimethylcyclopentane
1-*trans*-2-*cis*-3-Trimethylcyclopentane
1-*trans*-2-*cis*-4-Trimethylcyclopentane
1,1,2-Trimethylcyclopentane
1,1,3-Trimethylcyclohexane
1-*trans*-2-*trans*-4-Trimethylcyclohexane

Benzene
Toluene
Ethylbenzene
o-Xylene
m-Xylene
p-Xylene
N-propylbenzene
Isopropylbenzene

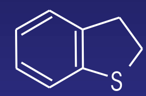
1-Methyl-2-ethylbenzene
1-Methyl-3-ethylbenzene
1-Methyl-4-ethylbenzene
1,2,3-Trimethylbenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
tert-Butylbenzene
1,2,3,4-Tetramethylbenzene
Tetrahydronaphthalene
Naphthalene
1-Methylnaphthalene
2-Methylnaphthalene
5-Methyltetrahydronaphthalene
6-Methyltetrahydronaphthalene

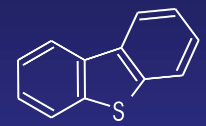
Methanethiol
Ethanethiol
2-Thiapropane
2-Propanethiol
2-Methyl-2-propanethiol
2-Thiabutane
1-Propanethiol
3-Methyl-2-thiabutane
2-Butanethiol
2-Methyl-1-propanethiol
3-Thiapentane
2-Thiapentane
1-Butanethiol
2-Methyl-2-butanethiol
3,3-Dimethyl-2-thiabutane
2-Methyl-3-thiapentane
3-Methyl-2-butanethiol
2-Pentanethiol
3-Pentanethiol
3-Thiahexane
2,4-Dimethyl-3-thiapentane
2,2-Dimethyl-3-thiapentane
Thiacyclopentane
2-Thiahexane
2-Methyl-3-thiahexane
Cyclopentanethiol
2-Methylthiacyclopentane
4-Methyl-3-thiahexane
3-Methylthiacyclopentane
2-Hexanethiol
Thiacyclohexane
trans-2,5-Dimethylthiacyclopentane
cis-2,5-Dimethylthiacyclopentane
3-Thiaheptane
2-Methylthiacyclohexane
3-Methylthiacyclohexane
4-Methylthiacyclohexane
Cyclohexanethiol

C12 – 355 isomers
C40 – 6.2×10^{13} isomers

Petroleum – Minor Components of Major Importance

Sulfur (0.1-0.6%)

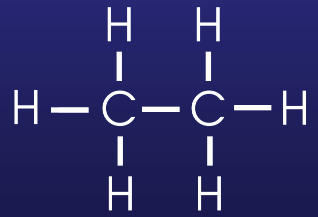




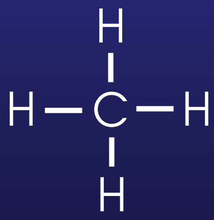
Polycyclic Aromatic Hydrocarbons (~ 1%)

Benzo[a]pyrene

Natural Gas (widely varies)



Ethane



Methane

Petrogenesis

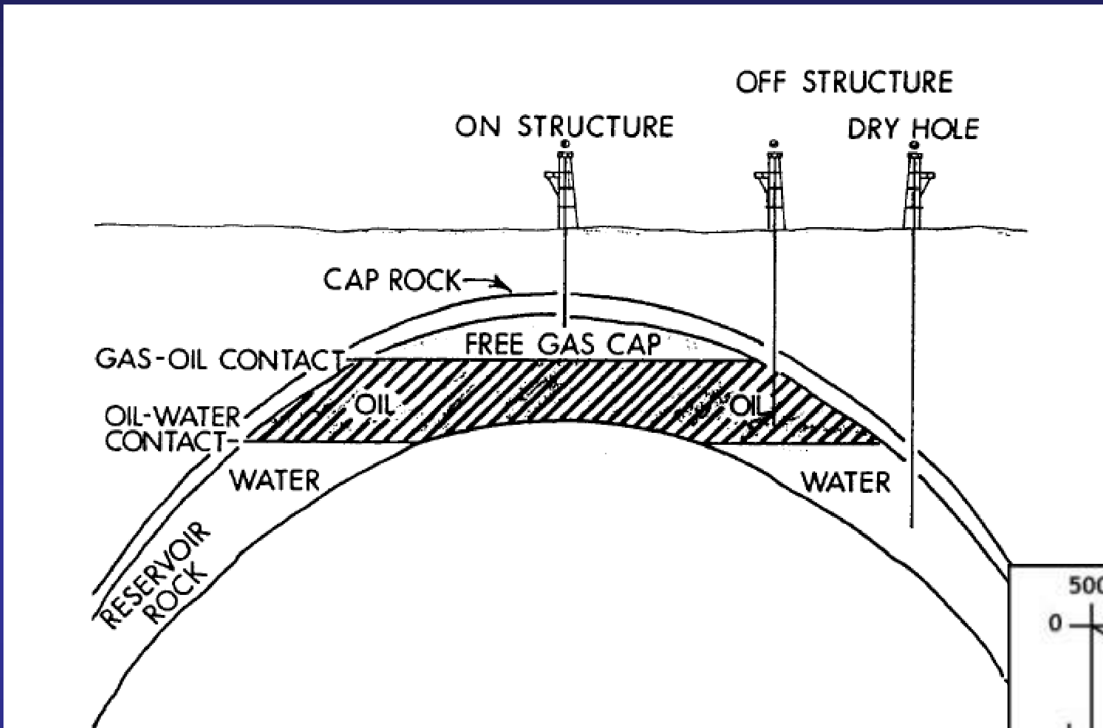
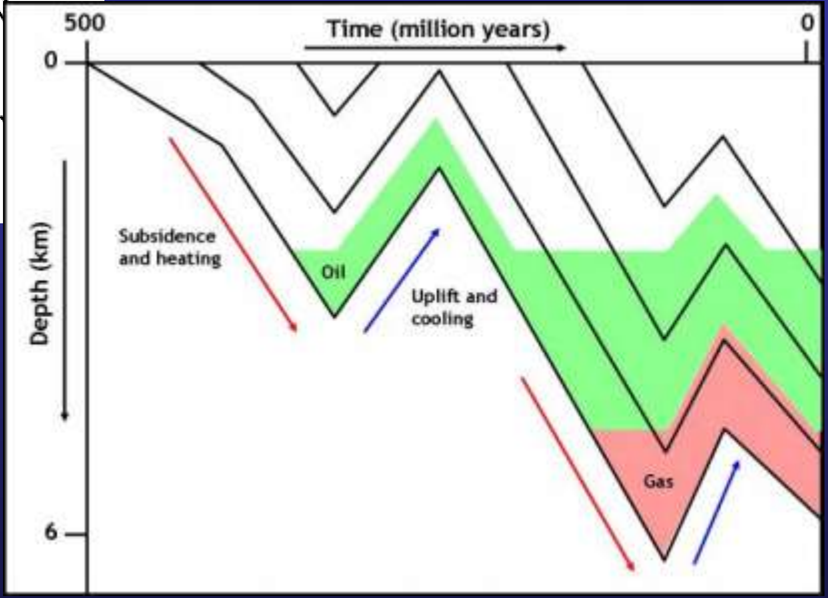
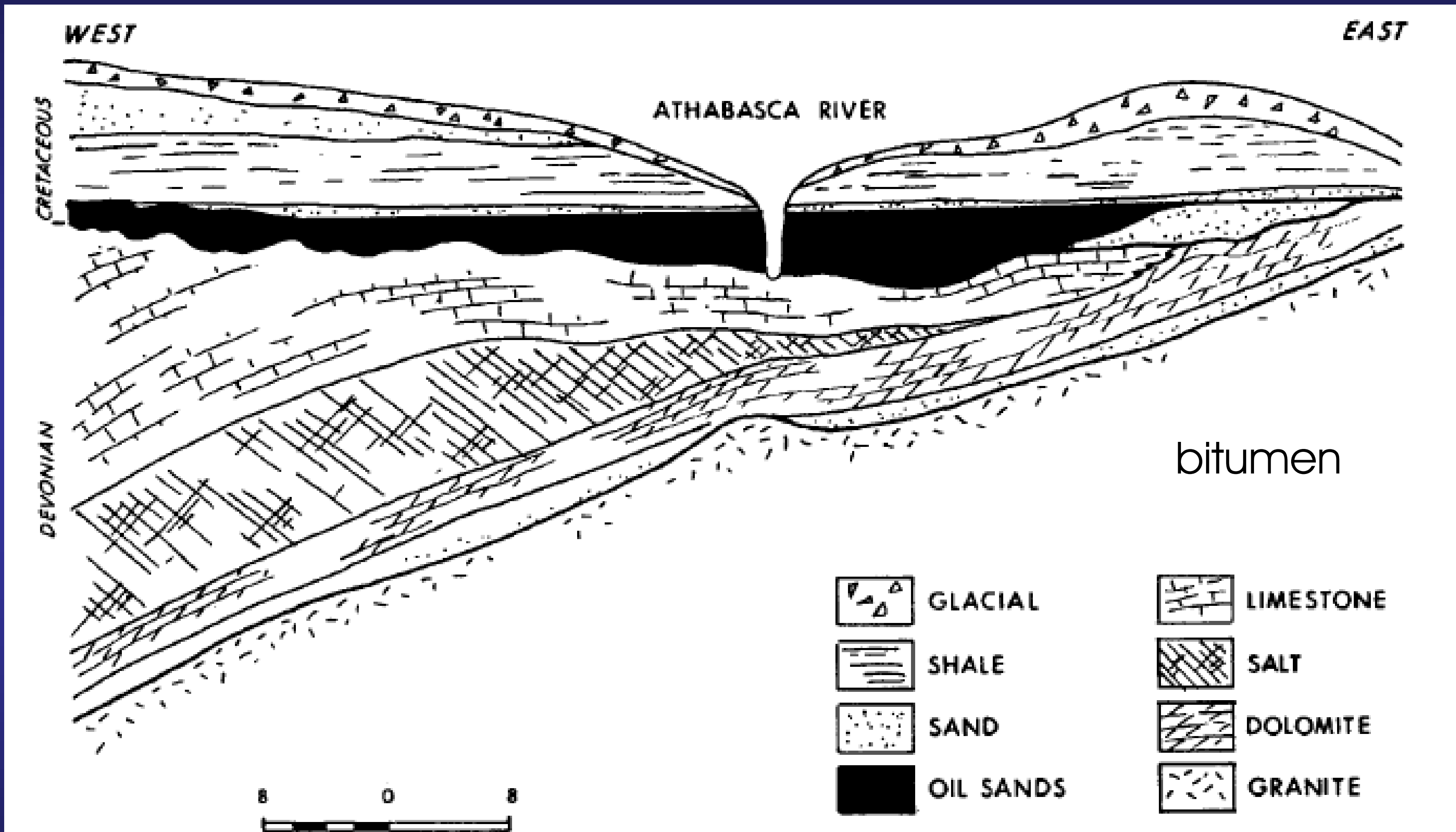


Fig. 11-5 *Details of a saturated pool*

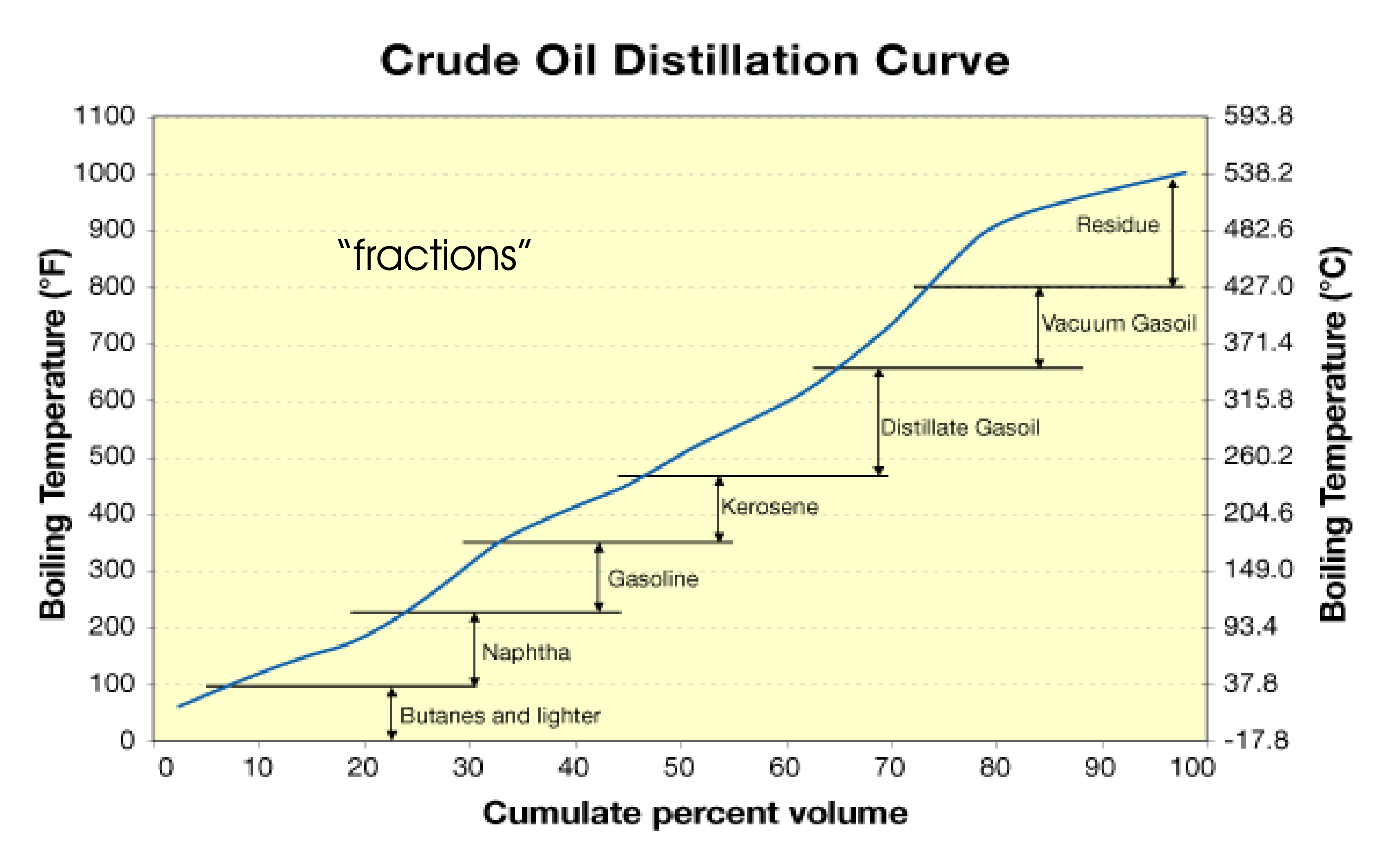


Oil Sands

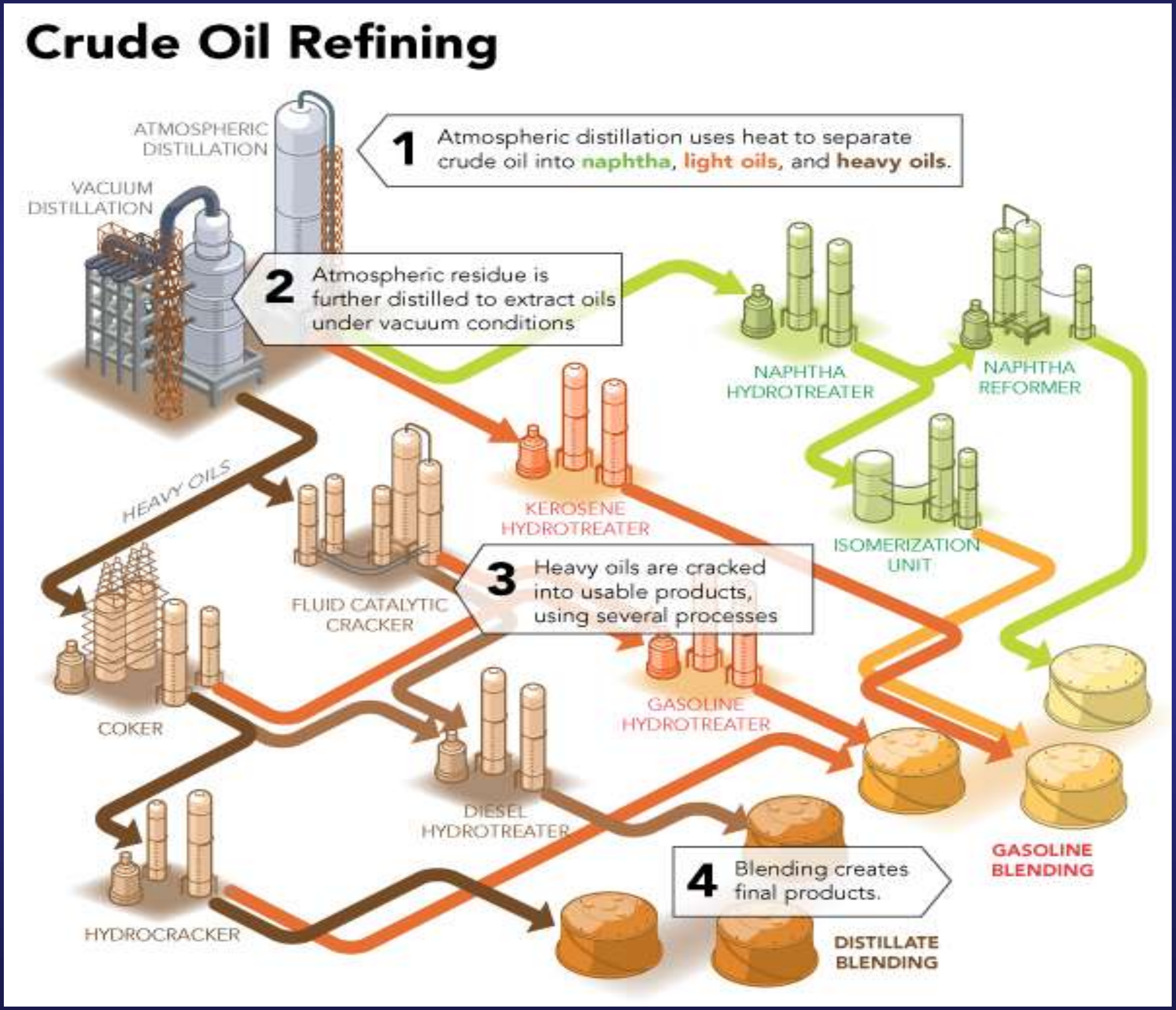


bitumen

Products


Crude Oil Distillation Curve
"fractions"
Boiling Temperature (°F)
Boiling Temperature (°C)
Cumulate percent volume
0
100
200
300
400
500
600
700
800
900
1000
1100
-17.8
37.8
93.4
149.0
204.6
260.2
315.8
371.4
427.0
482.6
538.2
593.8
0
10
20
30
40
50
60
70
80
90
100
Butanes and lighter
Naphtha
Gasoline
Kerosene
Distillate Gasoil
Vacuum Gasoil
Residue

Products

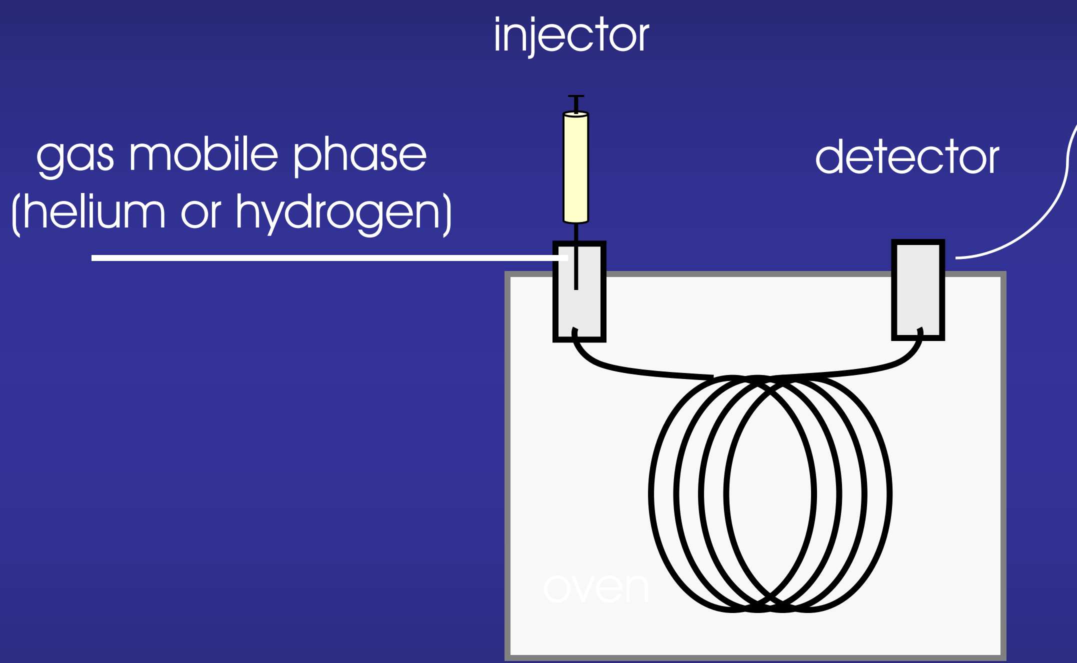

Crude Oil Refining
ATMOSPHERIC DISTILLATION
VACUUM DISTILLATION
1 Atmospheric distillation uses heat to separate crude oil into naphtha, light oils, and heavy oils.
2 Atmospheric residue is further distilled to extract oils under vacuum conditions
NAPHTHA HYDROTREATER
NAPHTHA REFORMER
KEROSENE HYDROTREATER
ISOMERIZATION UNIT
HEAVY OILS
FLUID CATALYTIC CRACKER
3 Heavy oils are cracked into usable products, using several processes
COKER
GASOLINE HYDROTREATER
DIESEL HYDROTREATER
GASOLINE BLENDING
4 Blending creates final products.
HYDROCRACKER
DISTILLATE BLENDING

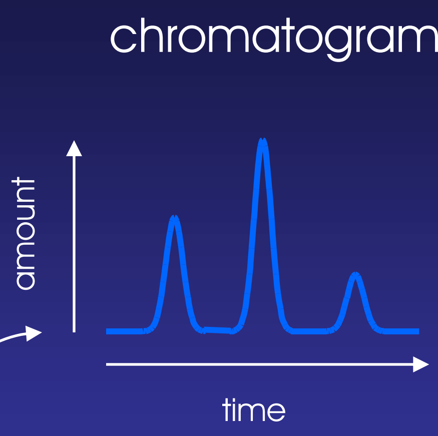
Typical Composition of Fuel Oils

- Gasoline
  - C4 to C12
  - Rich in straight and branched alkanes (paraffins), cycloalkanes (naphthenes), alkenes (olefins), and aromatics
- Kerosene (some jet fuels)
  - C12 to C20
  - Rich in straight and branched alkanes (paraffins), and cycloakanes (naphthenes)
- Diesel (Fuel Oil No.2)
  - C12 to C20
  - Rich in straight and branched alkanes (paraffins), cycloalkanes (naphthenes), aromatics
- IFOs (Fuel Oil No.6)
  - Blend of low boiling products and residuum
  - Alkanes, Aromatics, PAHs, NSOs

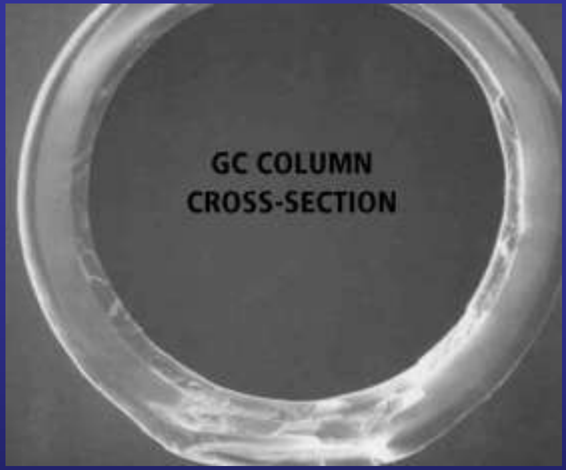
Chromatography – Charting the Crudes

Gas Chromatography (GC)

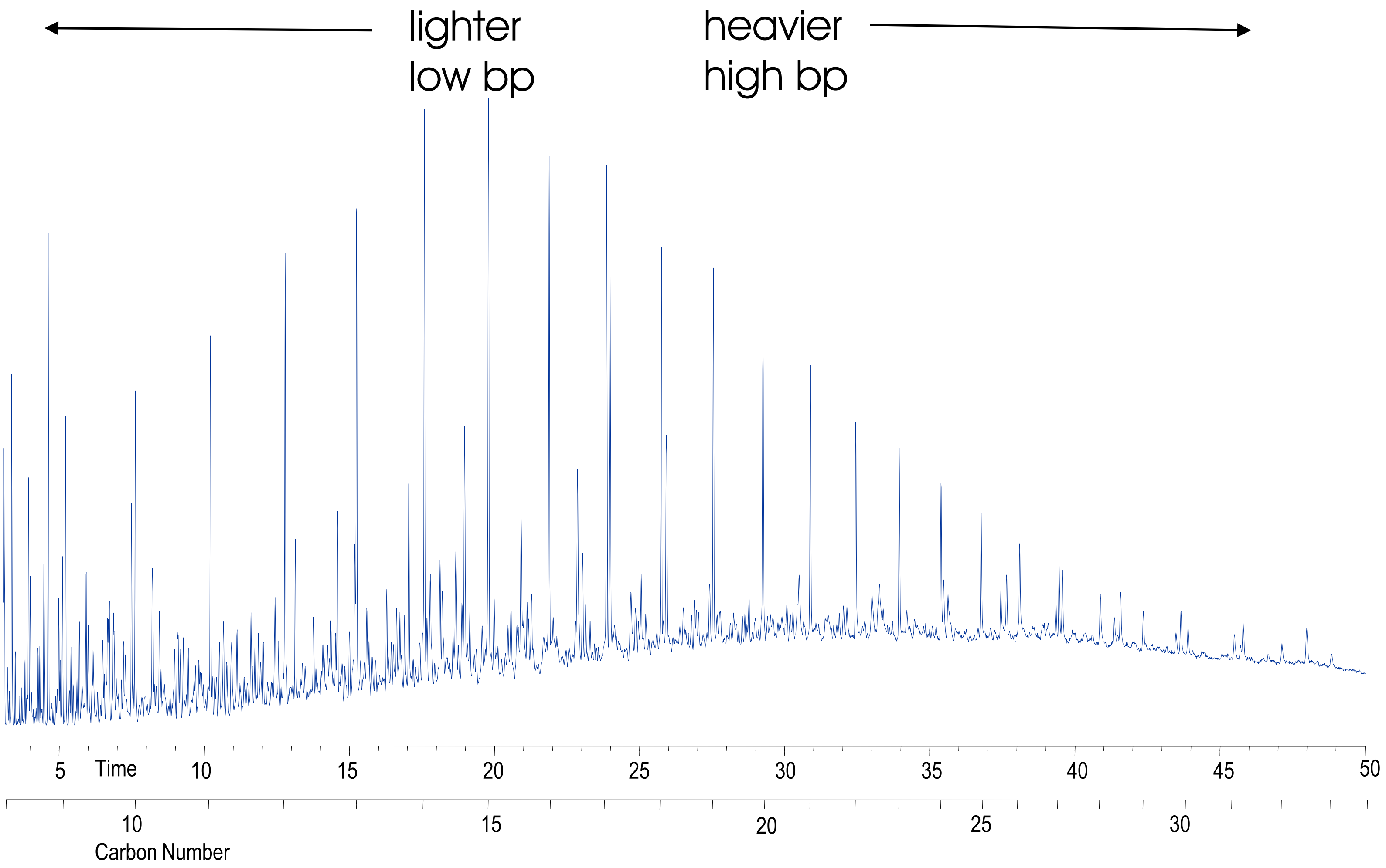




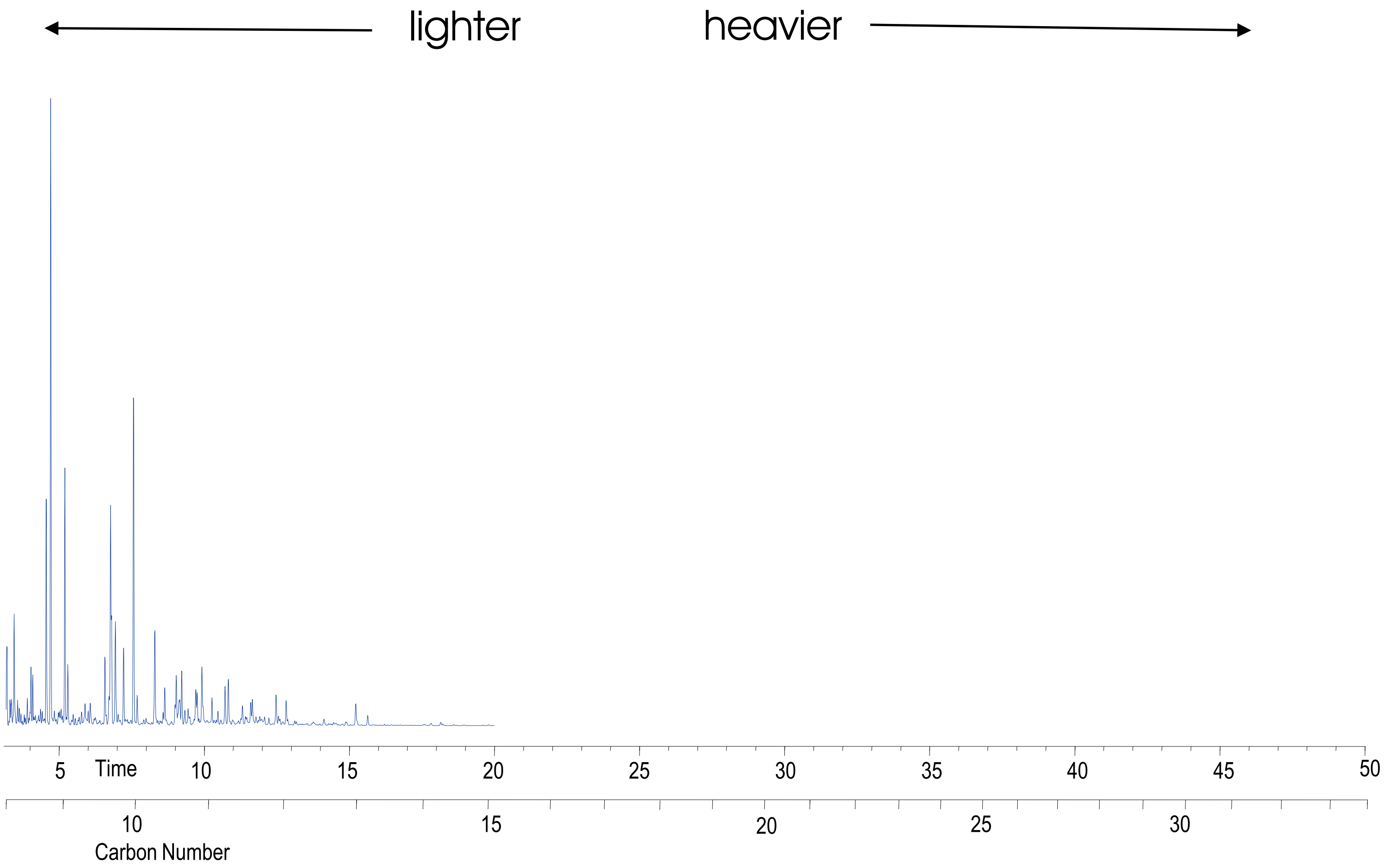
column with liquid polymer
(polydimethylsiloxane)
stationary phase



South Louisiana Crude

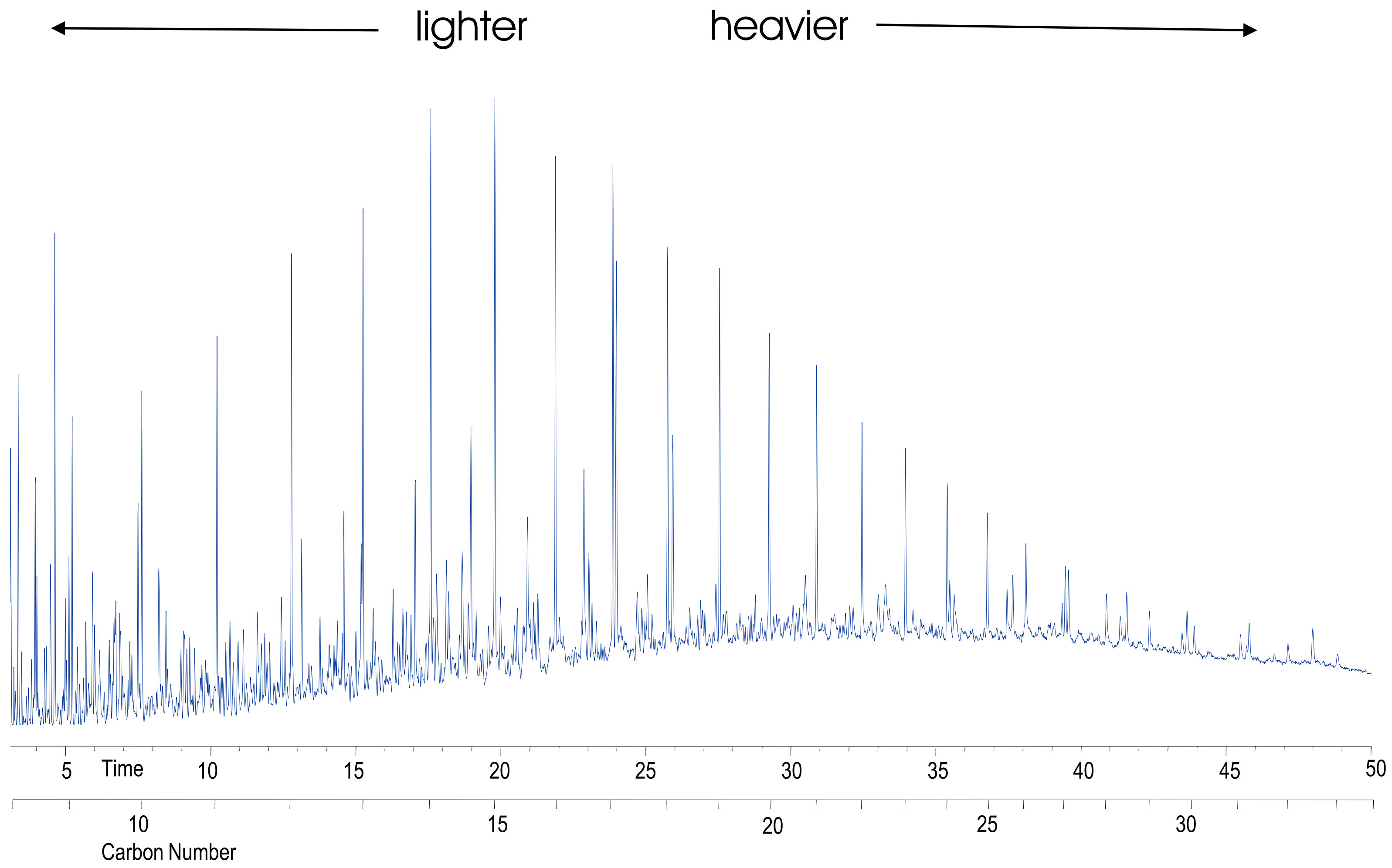


Gasoline



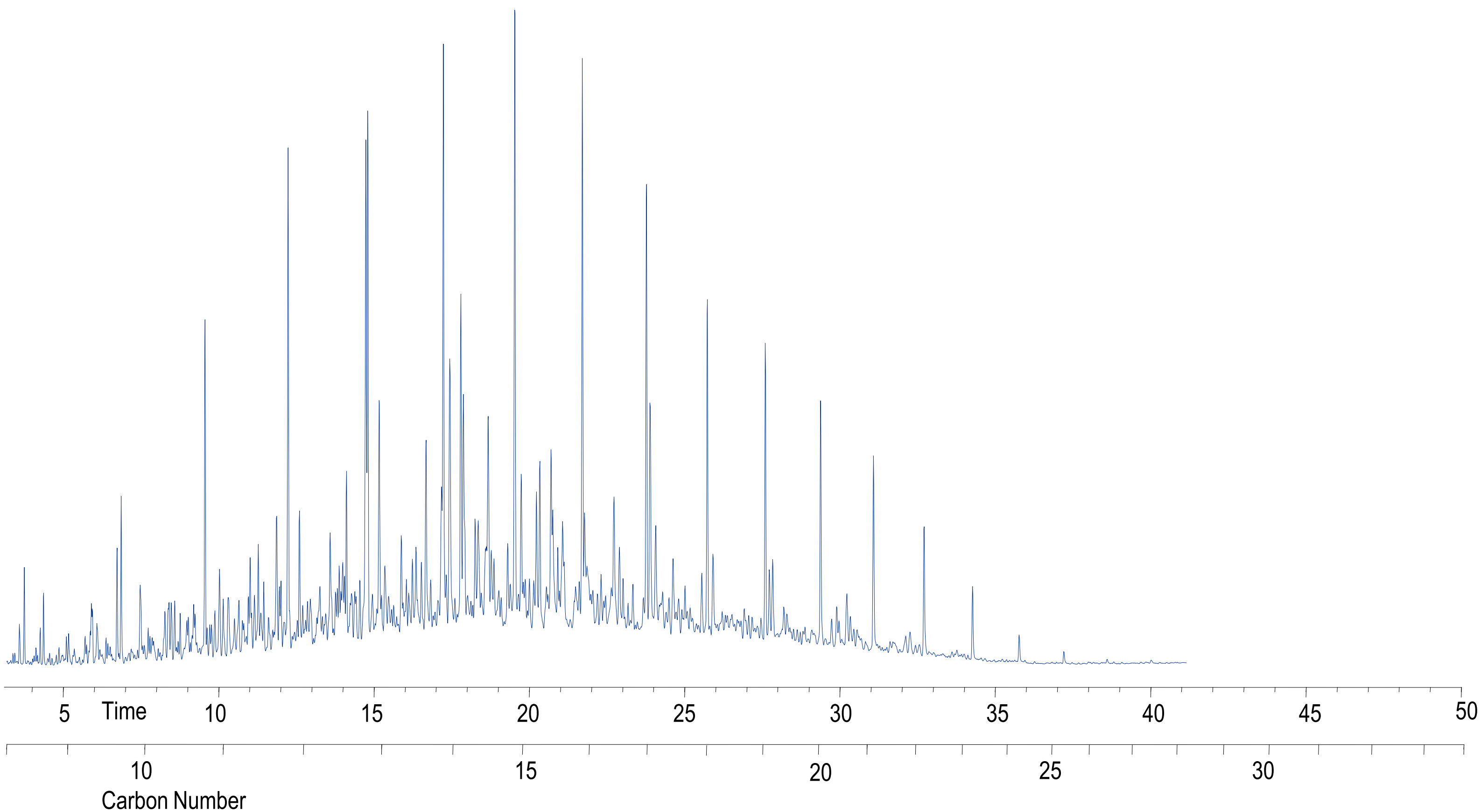
lighter
heavier
5
Time
10
15
20
25
30
35
40
45
50
10
15
20
25
30
Carbon Number

South Louisiana Crude

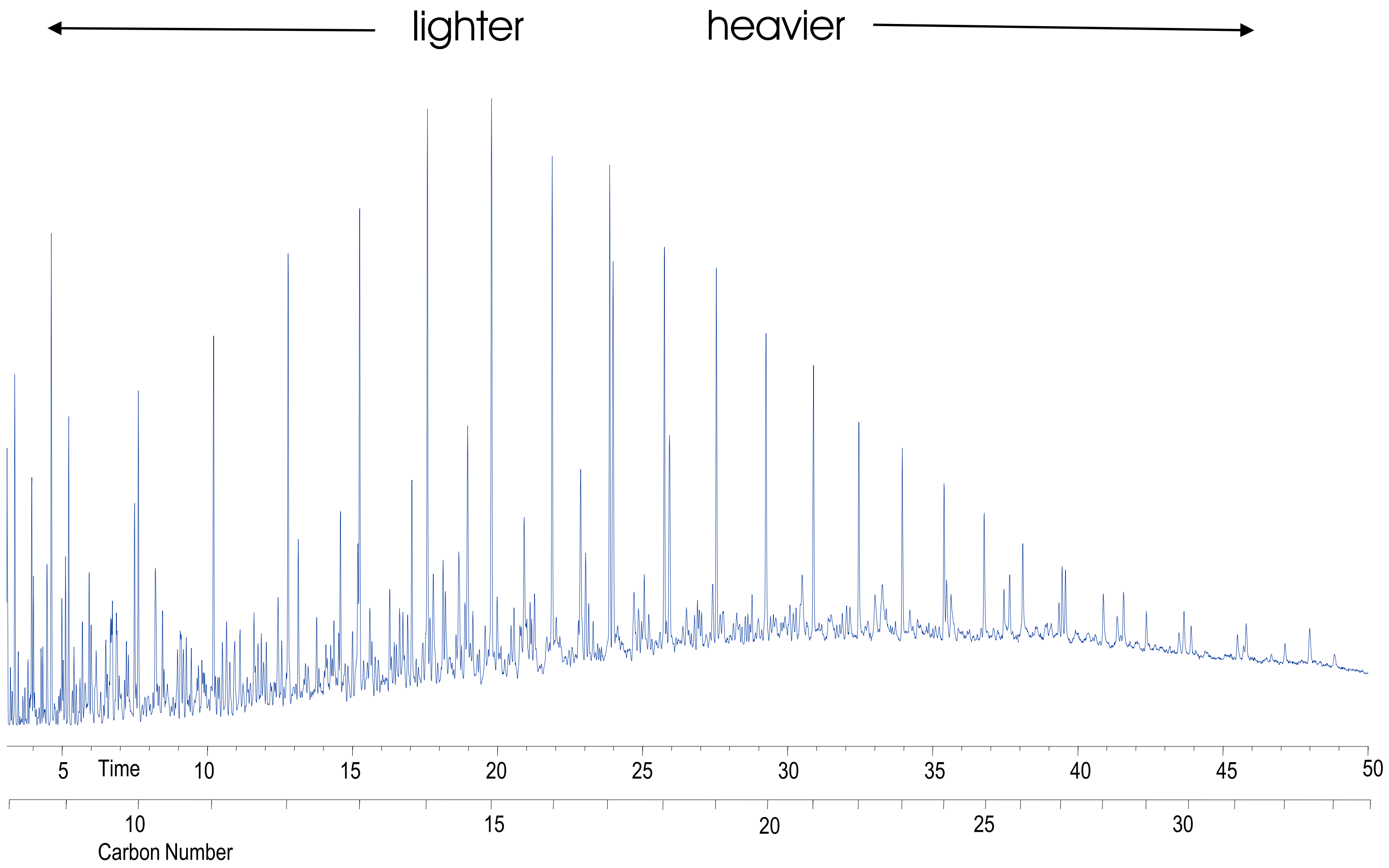


Diesel Fuel

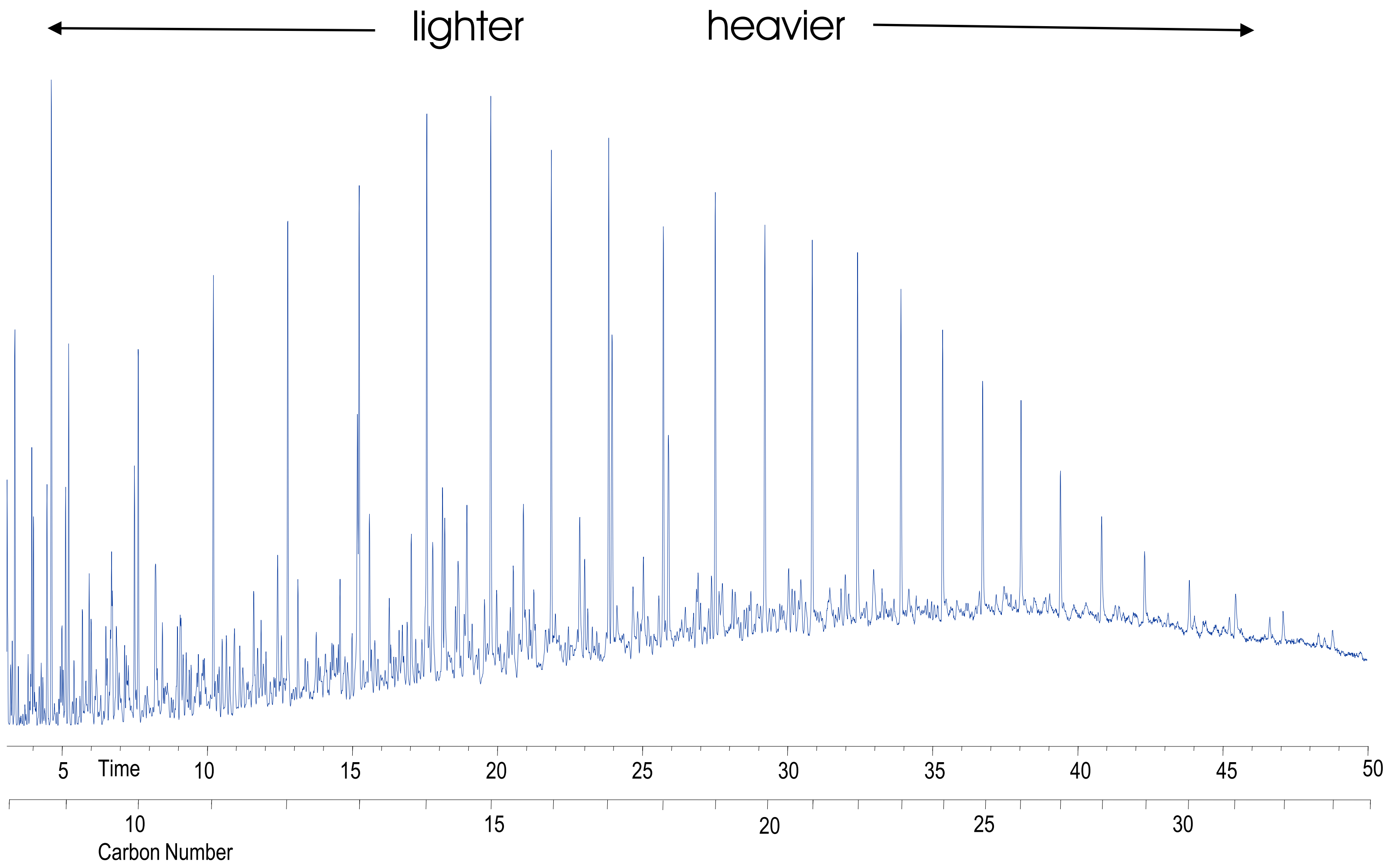
lighter heavier



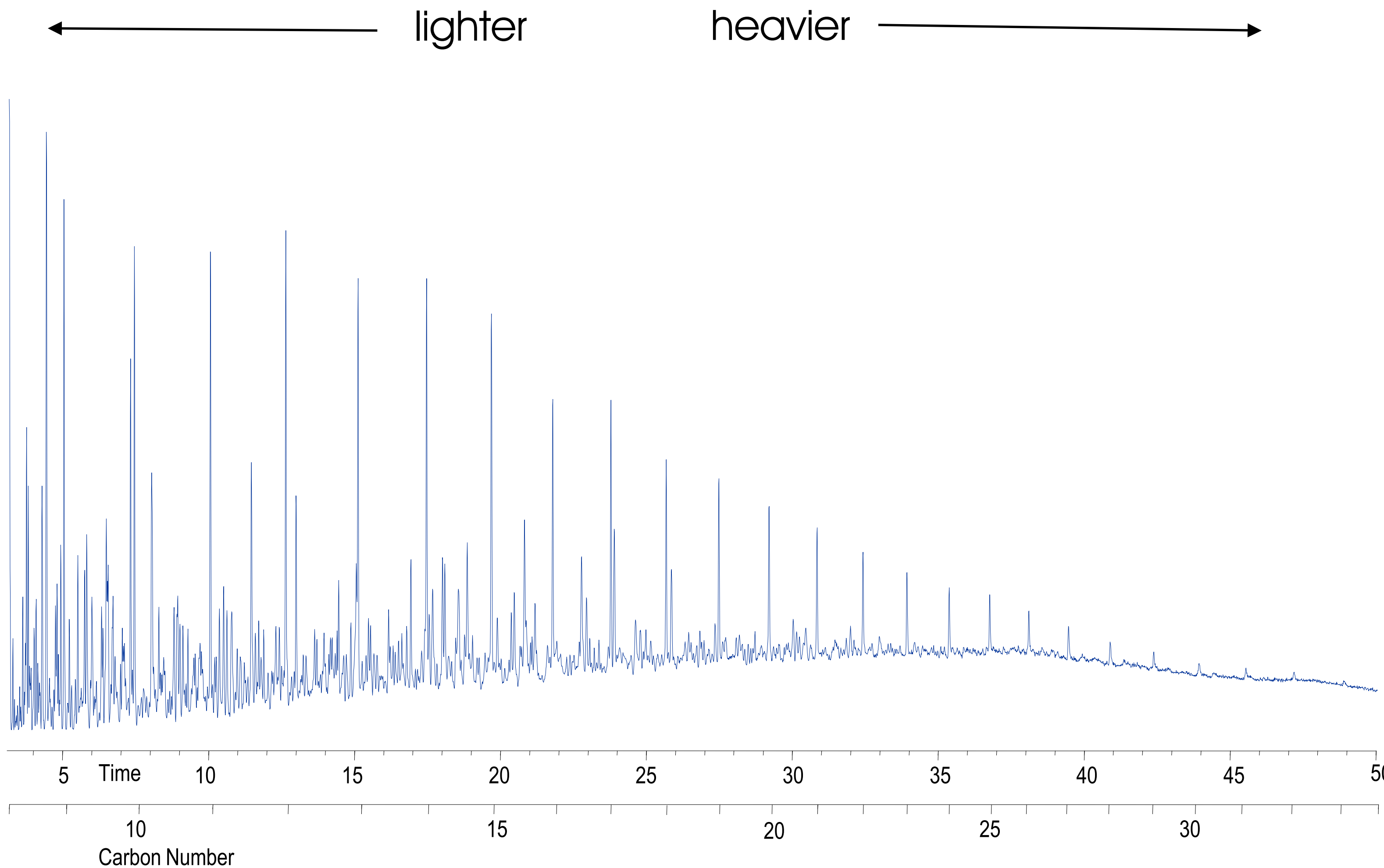
South Louisiana Crude



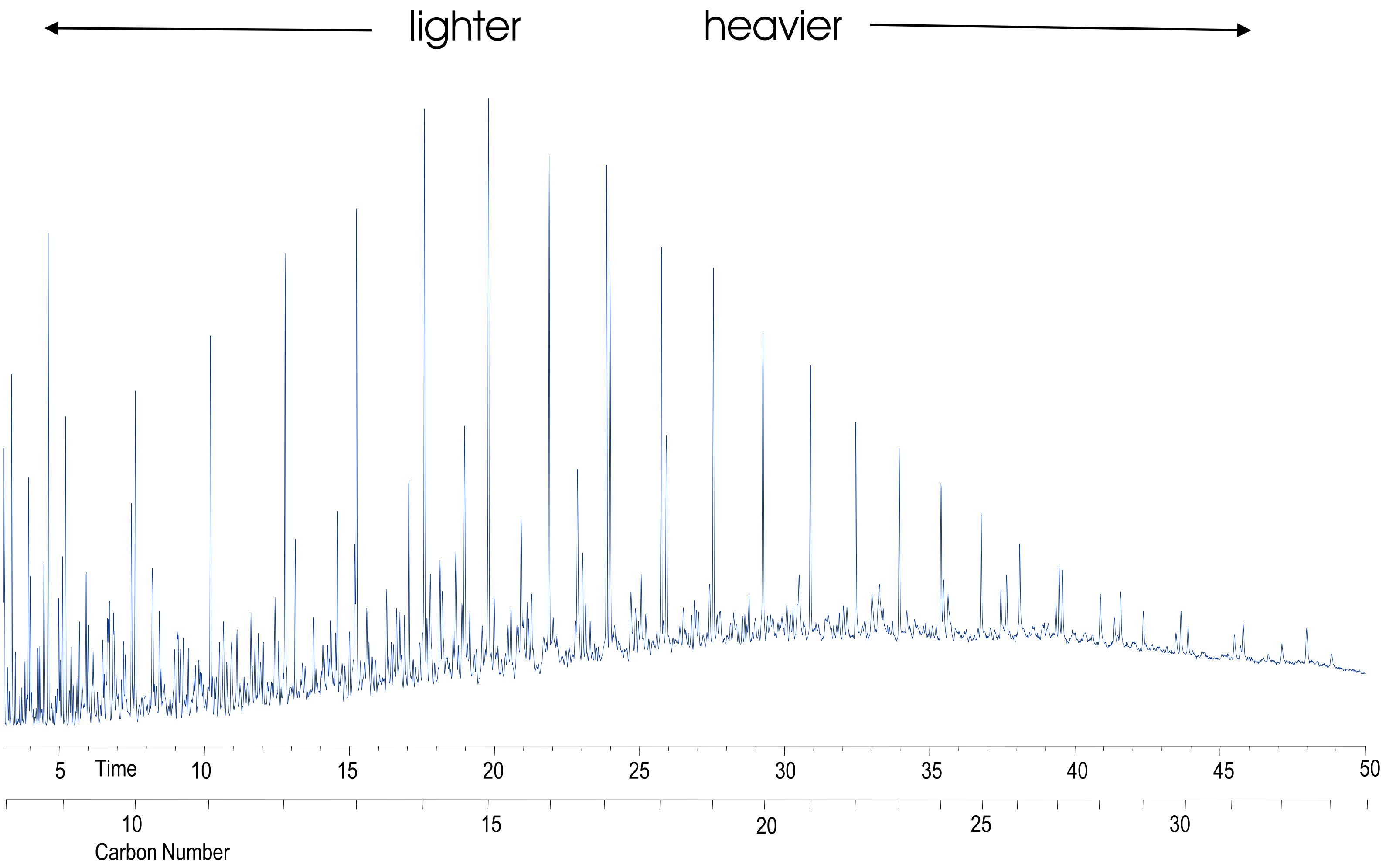
Exxon Valdez Cargo Oil



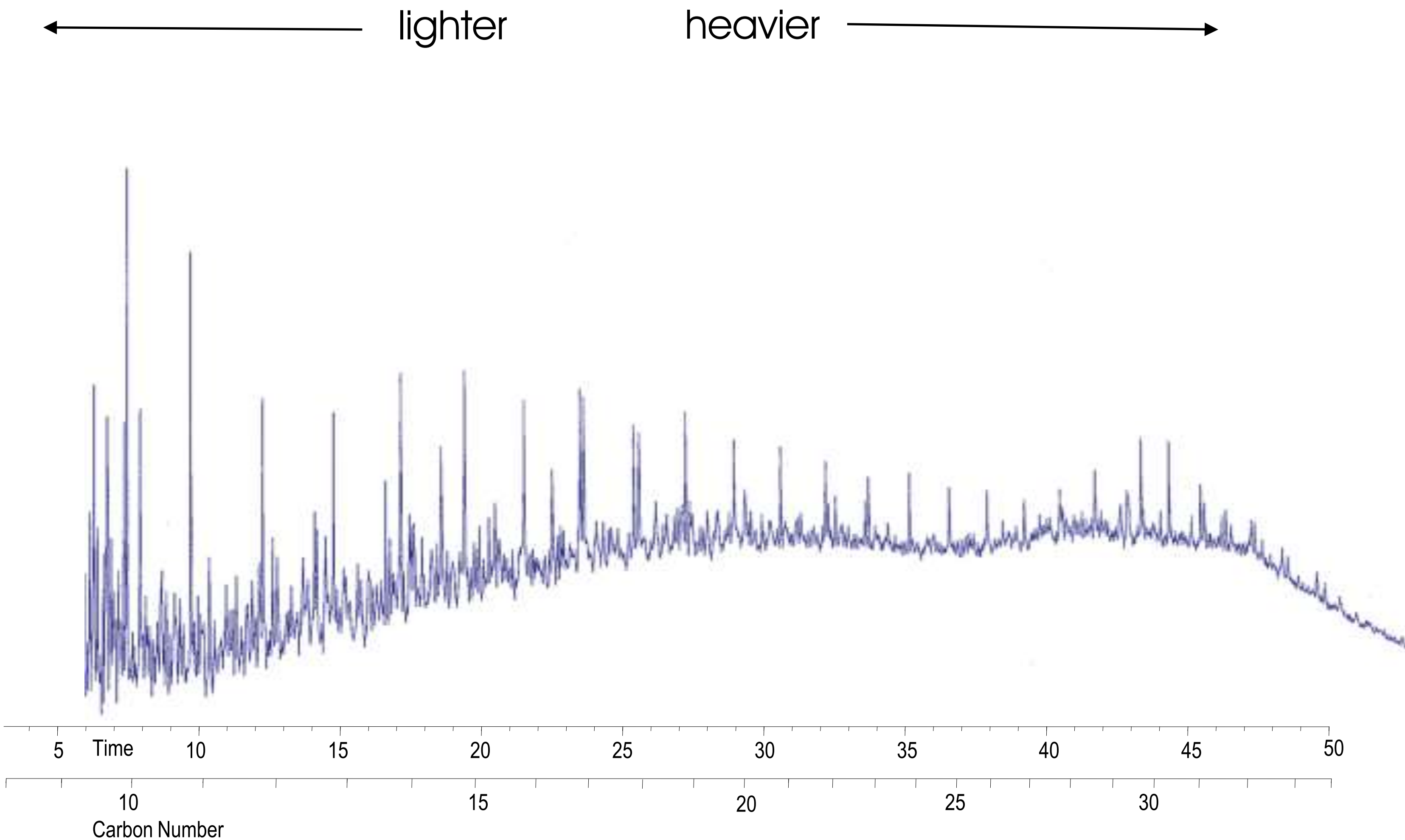
Bakken Crude



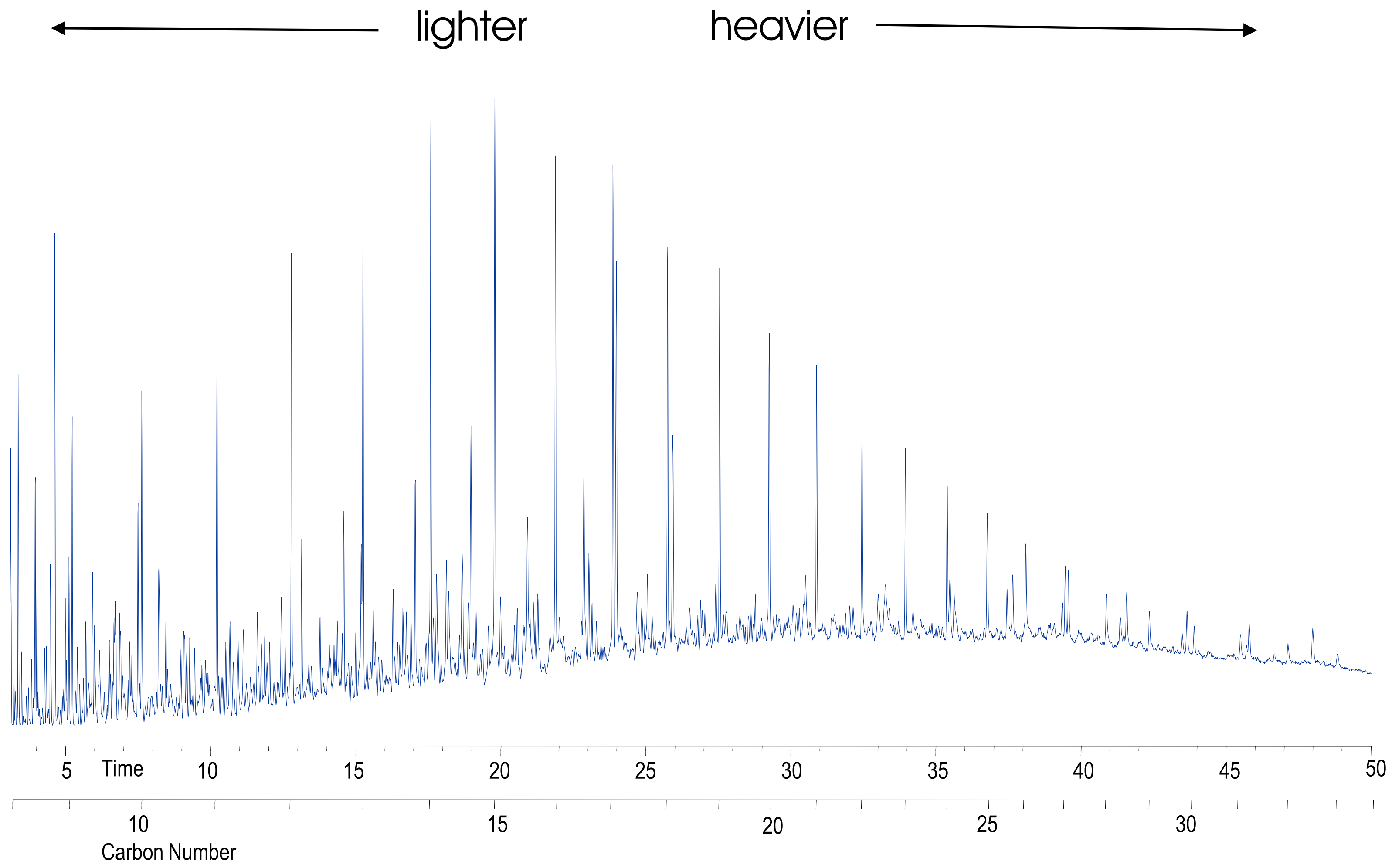
South Louisiana Crude



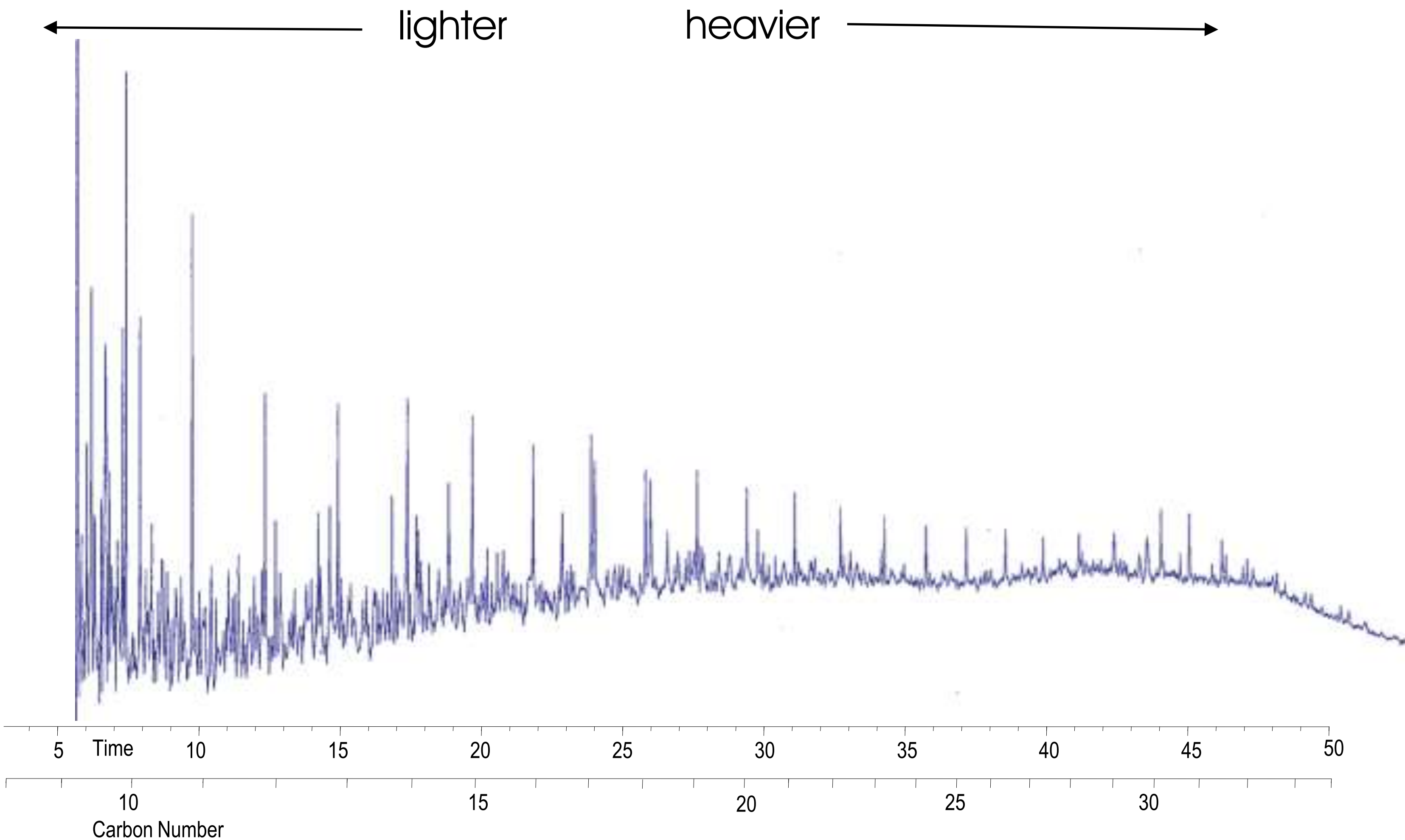
Kalamazoo River, Michigan 2010 (diluted bitumen “Dilbit”)



South Louisiana Crude



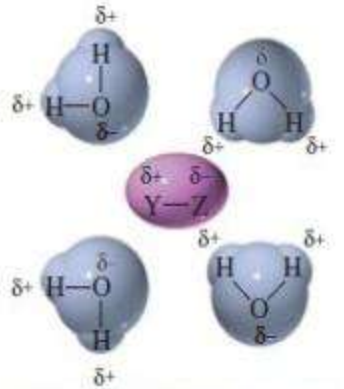
Mayflower, Arkansas 2013 (diluted bitumen)



Operational Measurements

Physical Measurements - Solubility

- How much solute can water hold
- It is not a measure of dissolution rate, but related to it
- Solubility of benzene -> 1800 mg/liter
- Solubility of hexane -> 10 mg/liter



solvation of a polar compound
$\overset{\delta+}{Y}-\overset{\delta-}{Z}$ by water

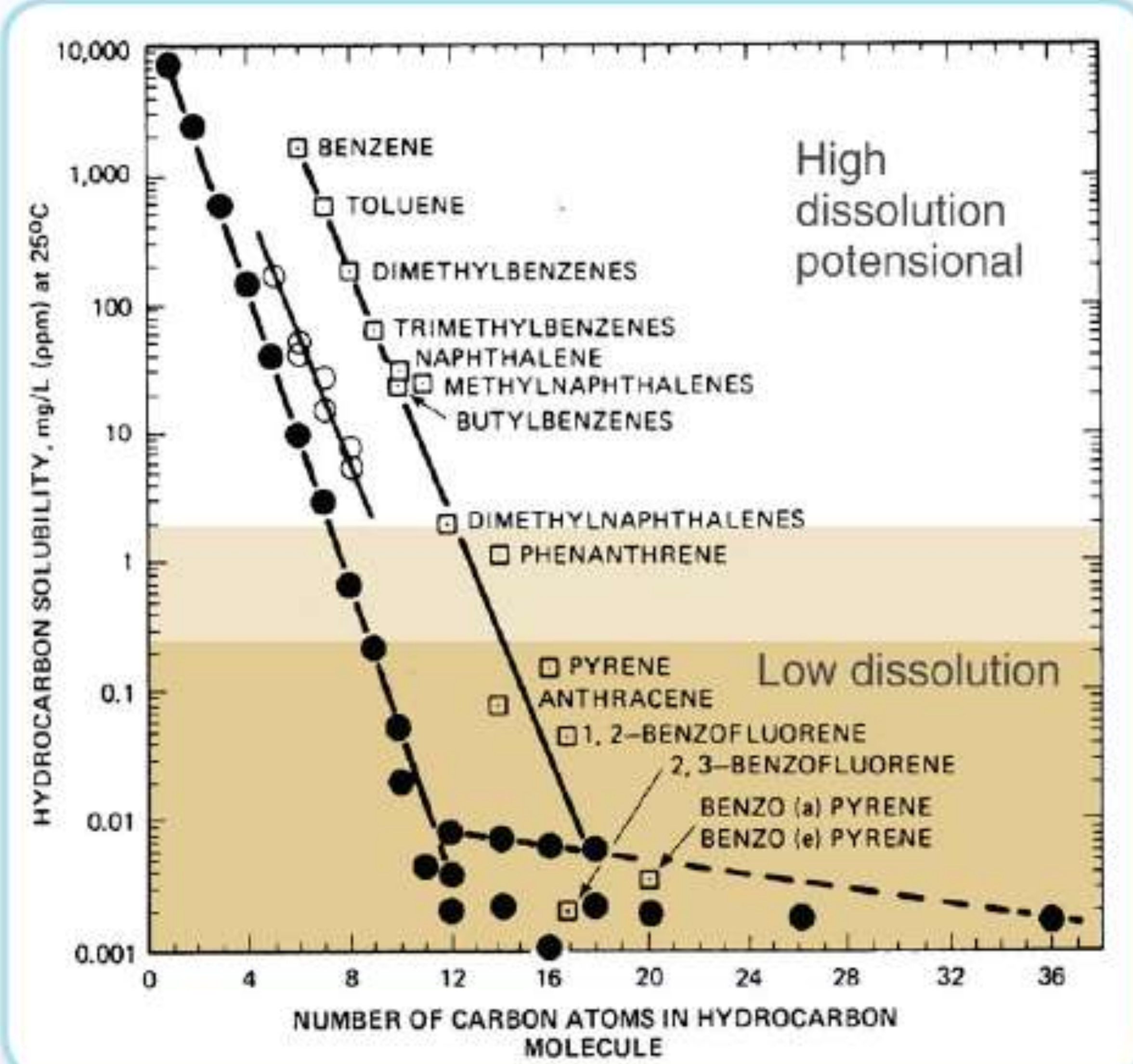


Figure 6: Solubility per carbon number for hydrocarbon molecules, (Modified from McAuliffe, 1987 IOSC - proc. Pp 275-288)

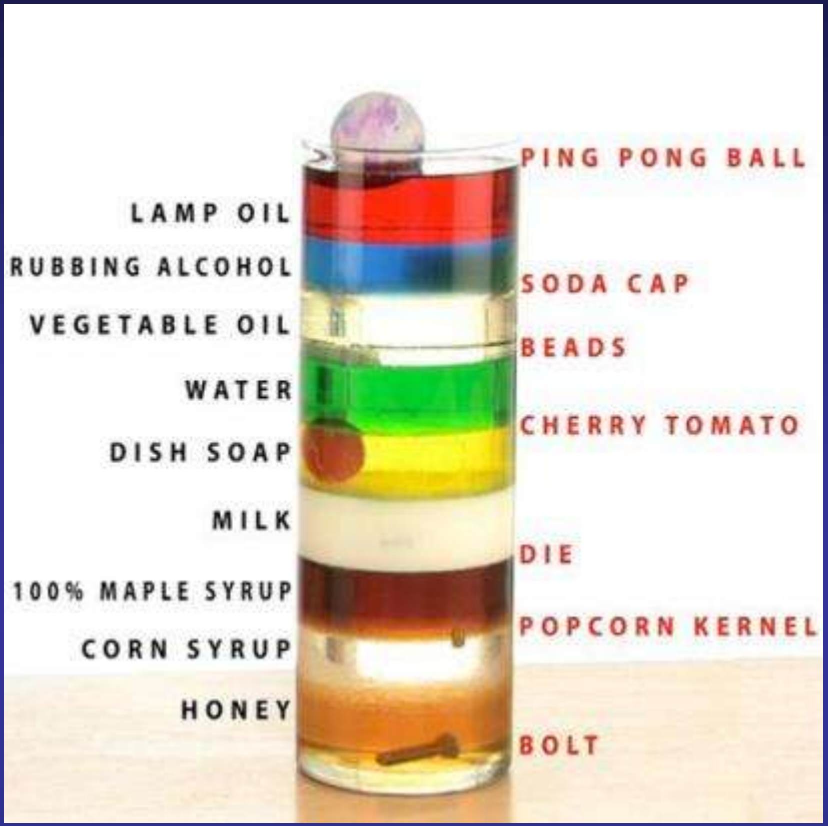
Lehr, B., S. Bristol, and A. Possolo. "Oil budget calculator—deepwater horizon, federal interagency solutions group, oil budget calculator science and engineering team, pp. A2. 1– A2. 10 (2010)."

Physical Measurements - Density

- Density (δ) is mass per unit volume e.g. g/mL.

- Specific gravity (SG) is the ratio of density of oil to the density of freshwater.

- API Gravity = (141.5/SG@60F) - 131.5



Density

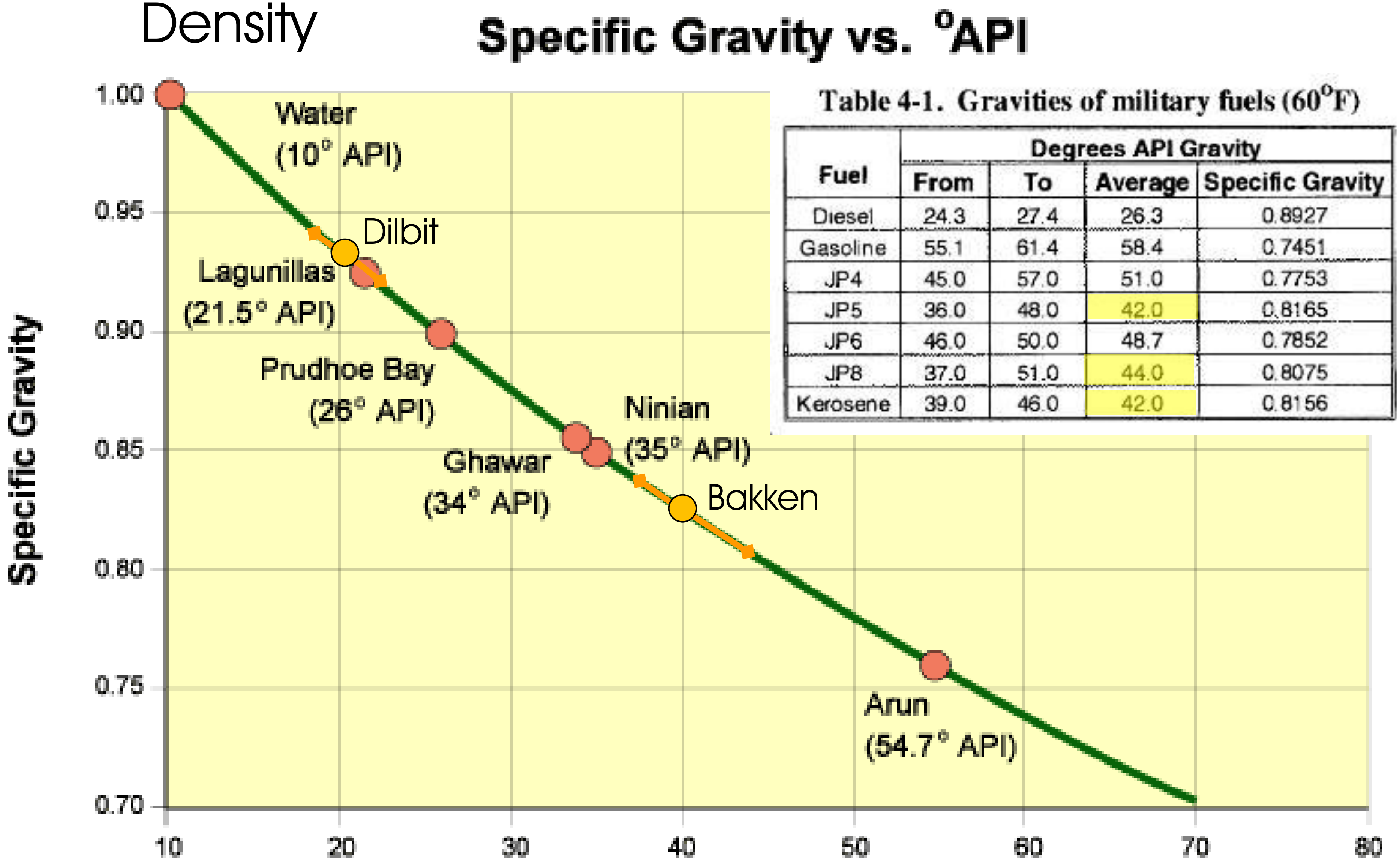


Table 4-1. Gravities of military fuels (60°F)

Fuel	Degrees API Gravity			
	From	To	Average	Specific Gravity
Diesel	24.3	27.4	26.3	0.8927
Gasoline	55.1	61.4	58.4	0.7451
JP4	45.0	57.0	51.0	0.7753
JP5	36.0	48.0	42.0	0.8165
JP6	46.0	50.0	48.7	0.7852
JP8	37.0	51.0	44.0	0.8075
Kerosene	39.0	46.0	42.0	0.8156

API Gravity = (141.5/SG@60F) - 131.5 **°API**

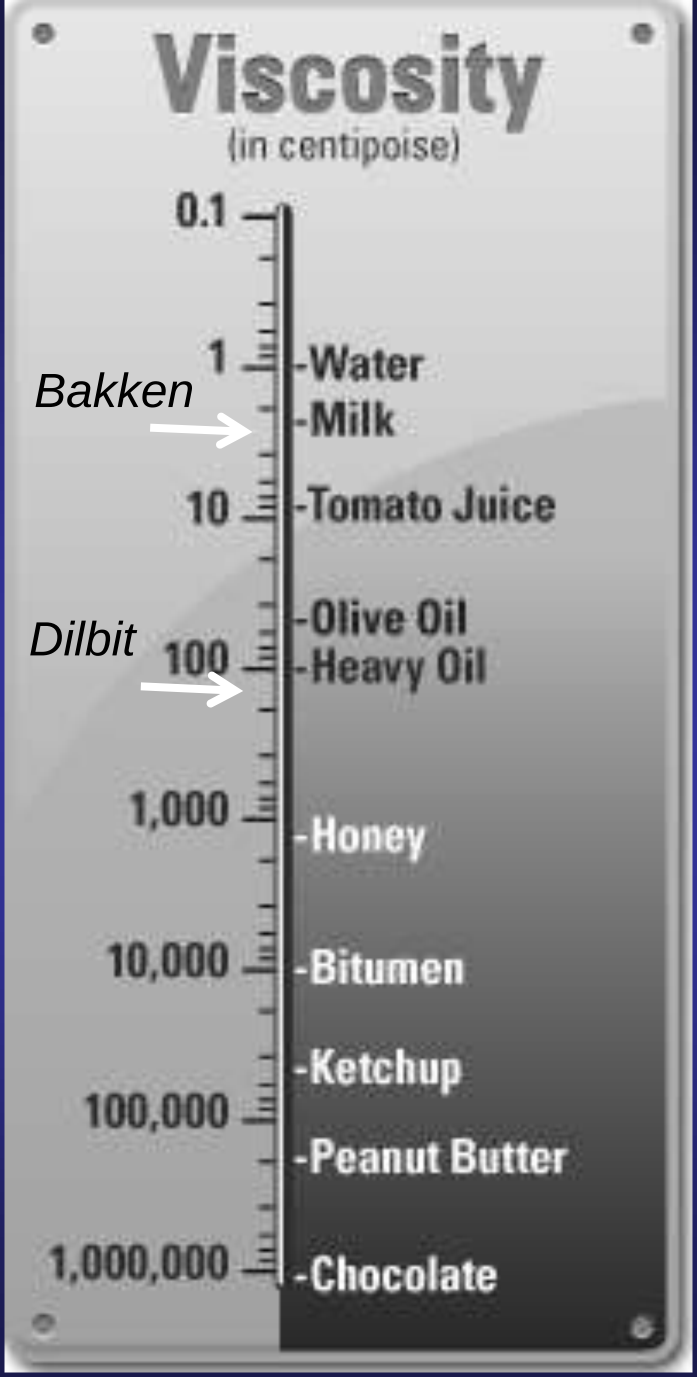
Physical Measurements - Viscosity

- A measure of a fluid's resistance to flow and spreading.
- Usually reported in centipoise (cP) or centistokes (cSt) ranging from 1 to 100,000
- Correlates imperfectly with density
- Viscosity is sensitive to temperature
- Viscosity increases with weathering

Viscosity

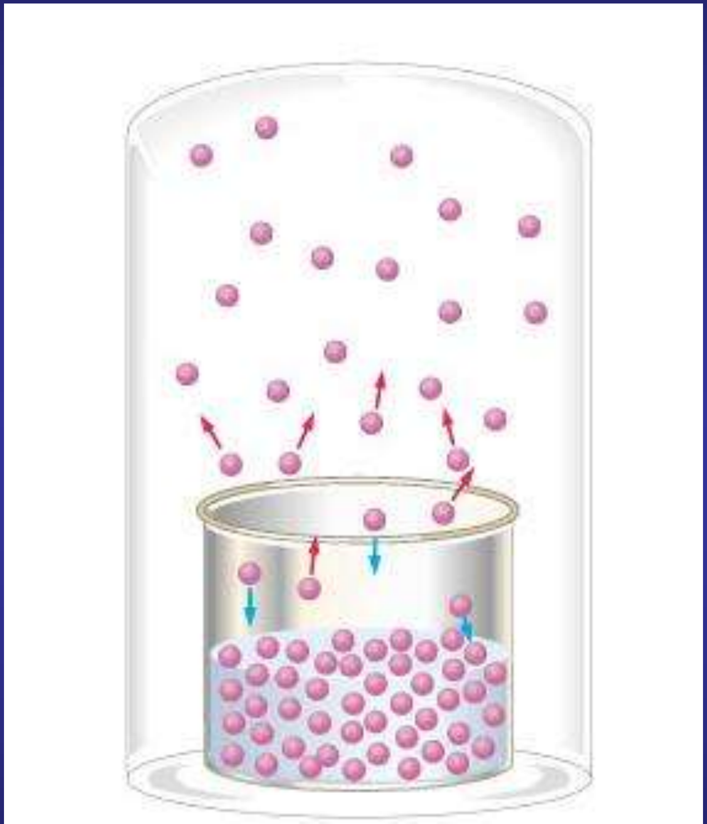
Viscosity (cP)	
Dilbit	~150
North Slope, AK	11.5
Brent	~6
South Louisiana Crude (MC 807)	4.8
Bakken Crude	3.3
Diesel	~2

“[Bakken] Looks like two-stroke oil mized with gasoline.”



Physical Measurements – Vapor Pressure

- How much vapor will be present in the space above its liquid form.
- Temperature dependent
- Not technically correct for mixtures, but a good guide.
- A liquid with a vapor pressure of 1 atm or 1 bar is boiling.
- "VOCs"

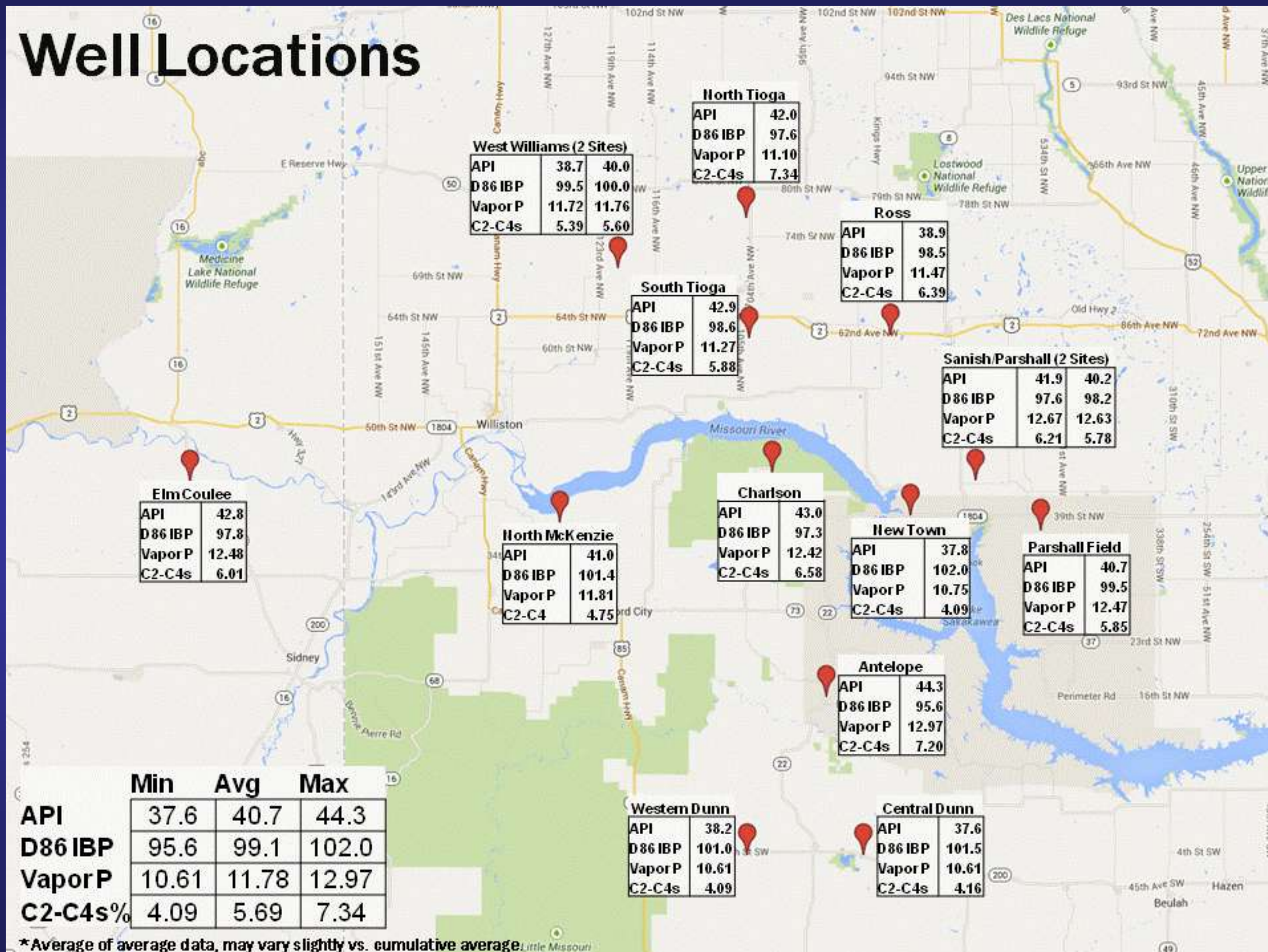


Volatility - Flashpoint

- A word about flashpoint.
  - Part of the determination of Packing Group within Hazard Class 3 (Flammable Liquids) 49 CFR 171-180
  - Several studies including DOT and NDPC agree that fresh Bakken is below detection.

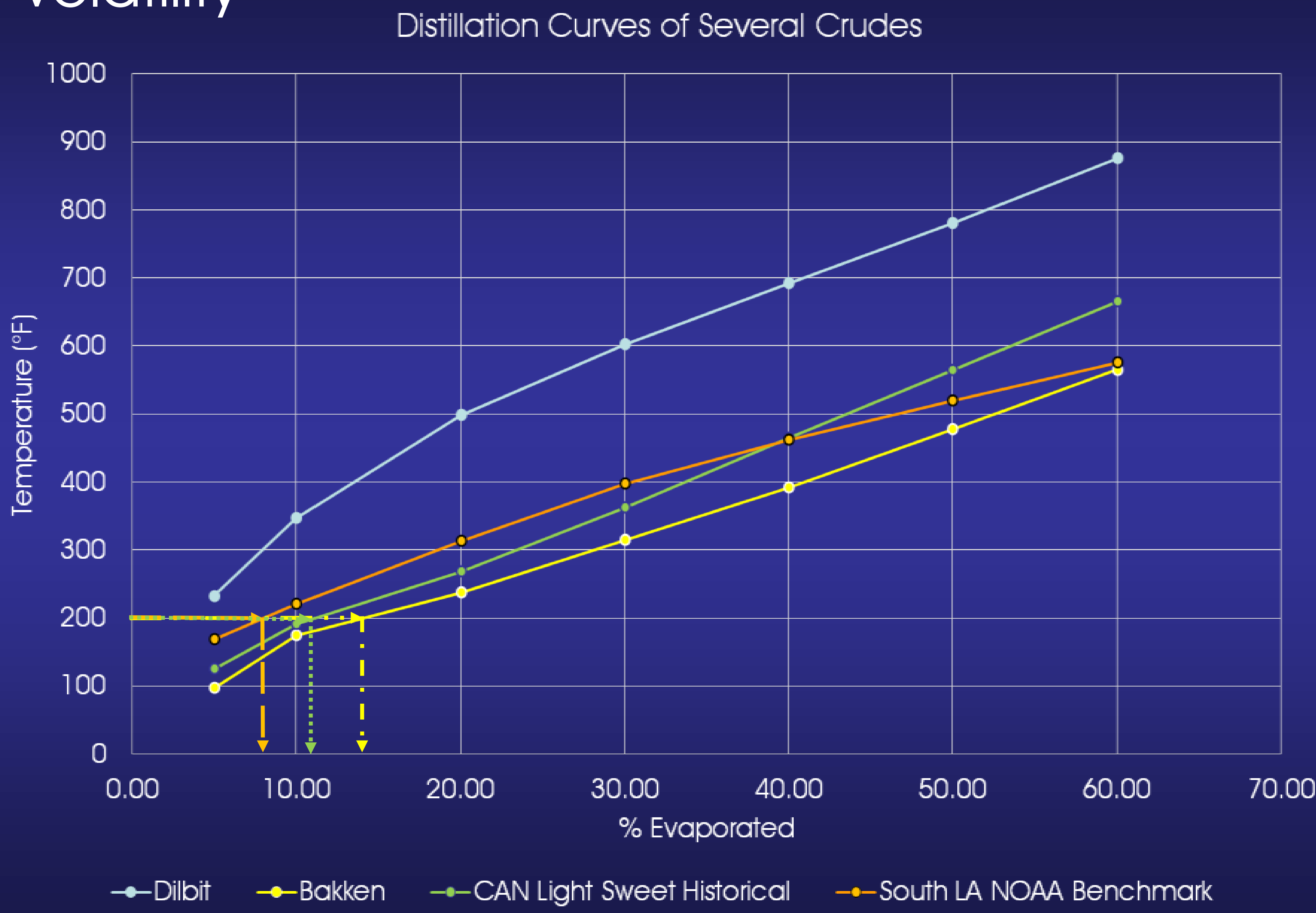
- Packing group is then determined by Initial Boiling Point. IBP cut off for Group I (Great Danger) is 95 °F. Significant #s of samples from this play test lower (in Group 1)
  - It is location and time dependent.
  - Those that test higher are very close.

Volatility



The North Dakota Petroleum Council Study on Bakken Crude Properties

Volatility



Distillation Curves of Several Crudes
Temperature (°F)
1000
900
800
700
600
500
400
300
200
100
0
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
% Evaporated
Dilbit
Bakken
CAN Light Sweet Historical
South LA NOAA Benchmark

Volatility – Notes from responses

- Bakken
  - Recoverable oil may only persist 4-8 hours.
  - Air monitoring important for safety

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Volatility – DOT Operation Safe Delivery - Bakken

"Prior to the launch of our sampling and analysis, FRA identified that most crude oil loading facilities were basing classification solely on a generic Safety Data Sheet) (SDS), formerly known as Material Safety Data Sheets (MSDS). " … "PHMSA observed that SDSs for crude oil were out-of-date with unverified information and provide ranges of chemical and physical property values instead of specific measured values. "

"Based upon the results obtained from sampling and testing of the 135 samples from August 2013 to May 2014, the majority of crude oil analyzed from the Bakken region displayed characteristics consistent with those of a Class 3 flammable liquid, PG I or II, with a predominance to PG I, the most dangerous class of Class 3 flammable liquids. "

Dissolved Gasses? - Bakken

Crude	% C2- C5
Louisiana Light Sweet	3.0
Brent	5.3
Bakken	7.2
Eagle Ford	8.3

Lab Result Summary (Bakken)

Sample Date Range	3/25 to 4/24/2014		
Total (152 Samples)	**Avg**	**Min**	**Max**
Ambient Temp (°F)*	34	10	65
API Gravity	41.0	36.7	46.3
Vapor Pressure (PSI)	11.7	8.9	14.4
D86 IBP (°F)	99.5 (PG II)	91.9 (PG I)	106.8 (PG II)
Light Ends (C2-C4s)	5.48	3.52	9.30
Rail (49 Samples)	**Avg**	**Min**	**Max**
Ambient Temp (°F)*	29	10	47
API Gravity	41.7	39.2	44.0
Vapor Pressure (PSI)	11.5	9.6	12.9
D86 IBP (°F)	100.3 (PG II)	96.7 (PG II)	104.1 (PG II)
Light Ends (C2-C4s)	4.95	3.91	6.44
Well (103 Samples)	**Avg**	**Min**	**Max**
Ambient Temp (°F)*	36	11	65
API Gravity	40.6	36.7	46.3
Vapor Pressure (PSI)	11.8	8.9	14.4
D86 IBP (°F)	99.1 (PG II)	91.9 (PG I)	106.8 (PG II)
Light Ends (C2-C4s)	5.76	3.52	9.30

*Some later samples missing Ambient Temp readings, may skew results colder

Volatility – Notes from responses

- Dilbit
  - Evaporates more than other heavy oils.
  - Air monitoring also important
  - What is left may sink.

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Oil Weathering Processes

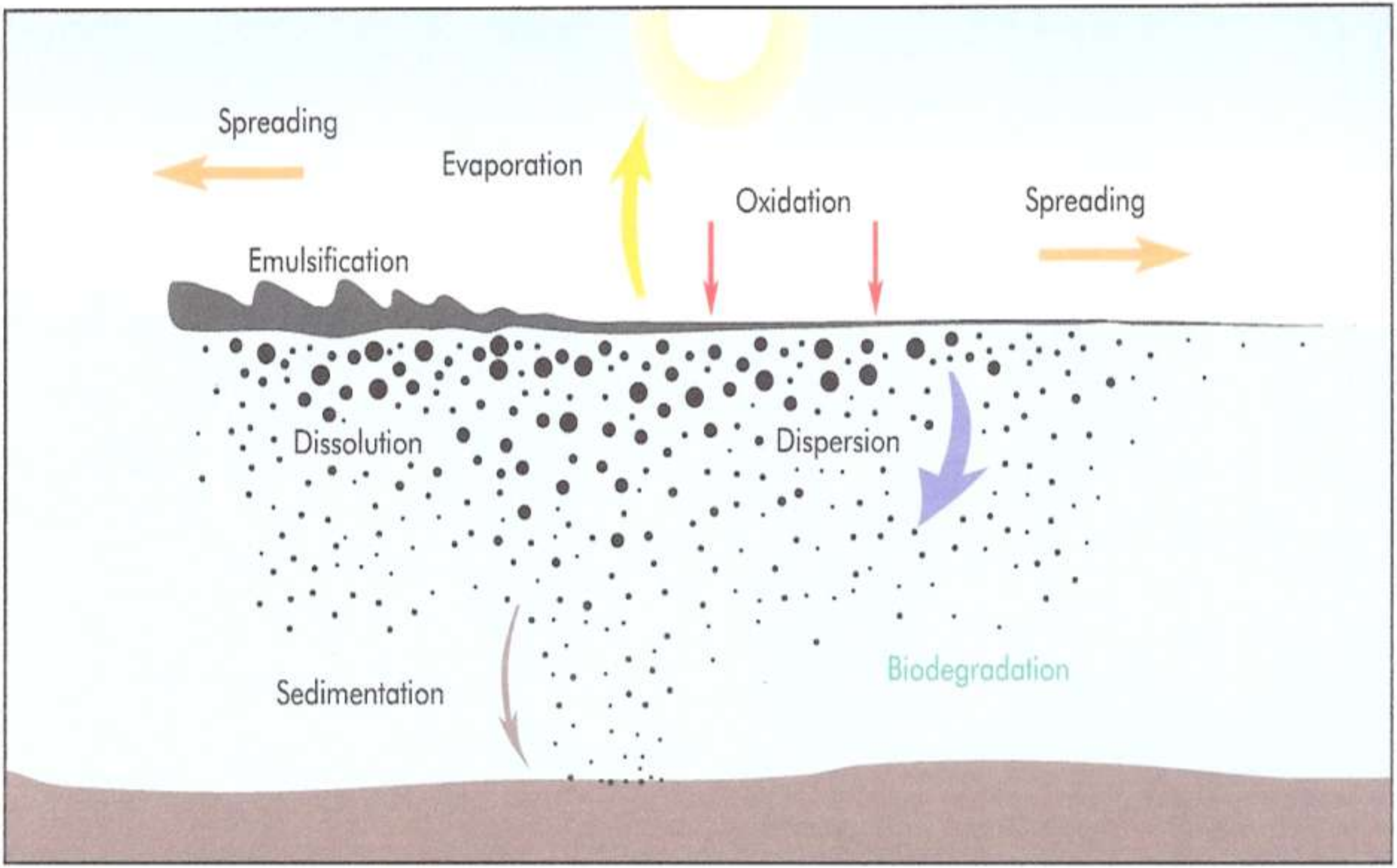

Figure 3: Processes acting on spilled oil.

ITOPF Technical Information Paper No.2 , Fate of Marine Oil Spills (http://www.itopf.com)

Corrosive?

AK Dept of Environmental Conservation

Summary

- Bakken and others from new shale plays are very light crudes.
  - Could contain dissolved natural gas in transport.
  - Bakken may not even be the lightest.
- Dilbit from oil sands and other bitumen products are mixtures of heavy petroleum and lighter diluents.
  - This mixture will act differently from other heavy crudes.
- While it is claimed that both are within the range of other crudes, they do push the limits and/or redefine their categories.
- Neither is fundamentally different from other products that are shipped, but they challenge our intuition of the characteristics of a “crude”.

Implications

Implications - Response

- Know the product spilled.
- Air monitoring may be indicated more often.
- Increasing diversity of crudes.

www.darrp.noaa.gov

Implications - Transport

- Geographic and modal specifics are dynamic.
- Are the regulations/testing specific enough?
- Are they aligned well with DOT?

Table 1 – Grade Classification per 46 CFR 30.10

Grade	Flashpoint (°F)	RVP (psia)	Venting
A	<80	>14	P/V
B	<80	8 to 14	P/V
C	<80	<8	P/V
D	80 to 150	N/A	Open
E	>150	N/A	Open

"The Coast Guard's design, construction and operating standards for Grade A and Grade B cargos are identical for cargoes with RVP below 25 psia."

BAKKEN CRUDE REVIEW AND REGULATORY ANALYSIS, CG-ENG-5, LT Murphy

Implications – Information?

- Where is this information coming from?

NIST

Questions?

gregory.hall@uscga.edu

Work 860 – 444 – 8624

Cel 860 – 867 - 6371