Petroleum Refining

The Genesis of Our Profession

Thomas A. Adams II
McMaster University
Department of Chemical Engineering
McMaster Advanced Control Consortium
McMaster Institute for Energy Studies

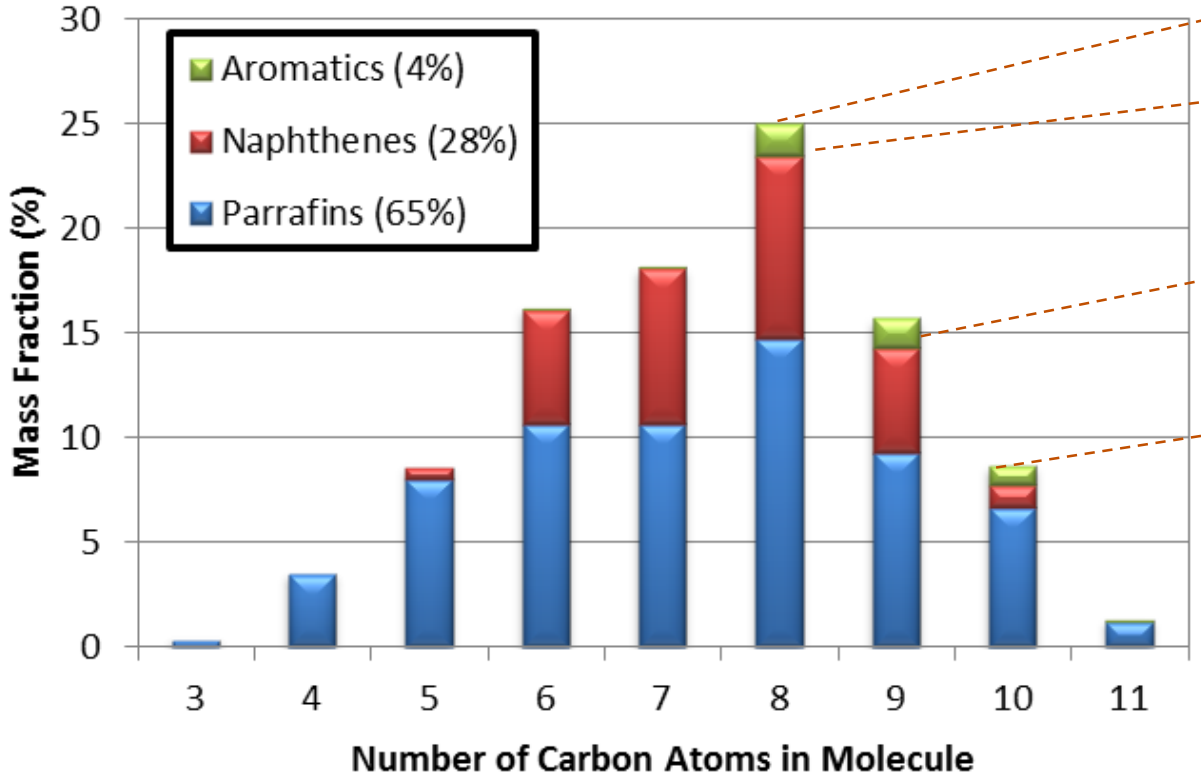
Lecture 5.1 – 2018 Edition

1. Transportation fuels

Gasoline, Diesel, etc.

Gasoline: What's in it?

- Blend of ~300 hydrocarbons of many types, plus additives
- Varies from oil to oil, process to process.



Molecules with 8 Carbons the most common
Thus we have the "octane" rating

Aromatics: contain aromatic rings
Benzenes, toluenes, xylenes, etc.
High octane rating

Naphthenes: cyclic alkanes
Cyclohexanes, cyclopentanes, etc.

Parrafins: Straight & branched alkanes
Butane, octane, ethylpentanes, etc
Ironically, low octane rating in general

Actual octane composition is 6-7 wt%

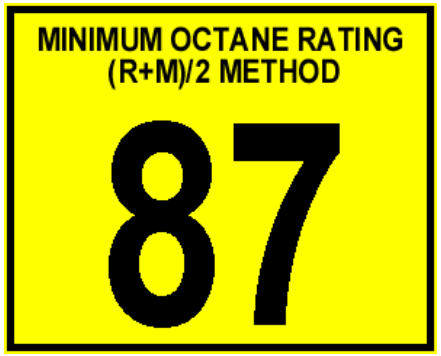
Notes: Data are from a well in Mongolia
This is the straight run gasoline cut (naphtha-
not actually gasoline yet, need to convert some parrafins to aromatics)
But carbon number distribution is similar.
More on that later…

McMaster University ENGINEERING
MACC McMaster Advanced Control Consortium

Sources: A. Sainbayar et al. / Journal of Petroleum Science and Engineering 46 (2005) 233–242

Octane Rating

- The "octane" rating is the ability to prevent knock
  - Knock is when spontaneous ignition of gas/air mixtures happen in the engine's cylinders.
    - You hear the knock when spontaneous and normal flames collide.
  - Determined by average of two standard tests in a special engine:
    - Research Octane Number – Measured at low engine speeds
    - Motor Octane Number – Measured at high engine speeds
    - Octane Rating = (R+M/2) → as mentioned on the gas pump
      - Define pure iso-octane as 100.
        - (n-octane is -10!!!)
      - 87 for regular unleaded, 89 for midgrade
      - 91-93 for various premium fuels
  - Octane rating is NOT power!!!
  - Only need the smallest rating that prevents knock.



Sources: BP "Fuel Your Mind" seminar, 2009 gasoline module
Ghosh 2009 – Chapter

Other contents

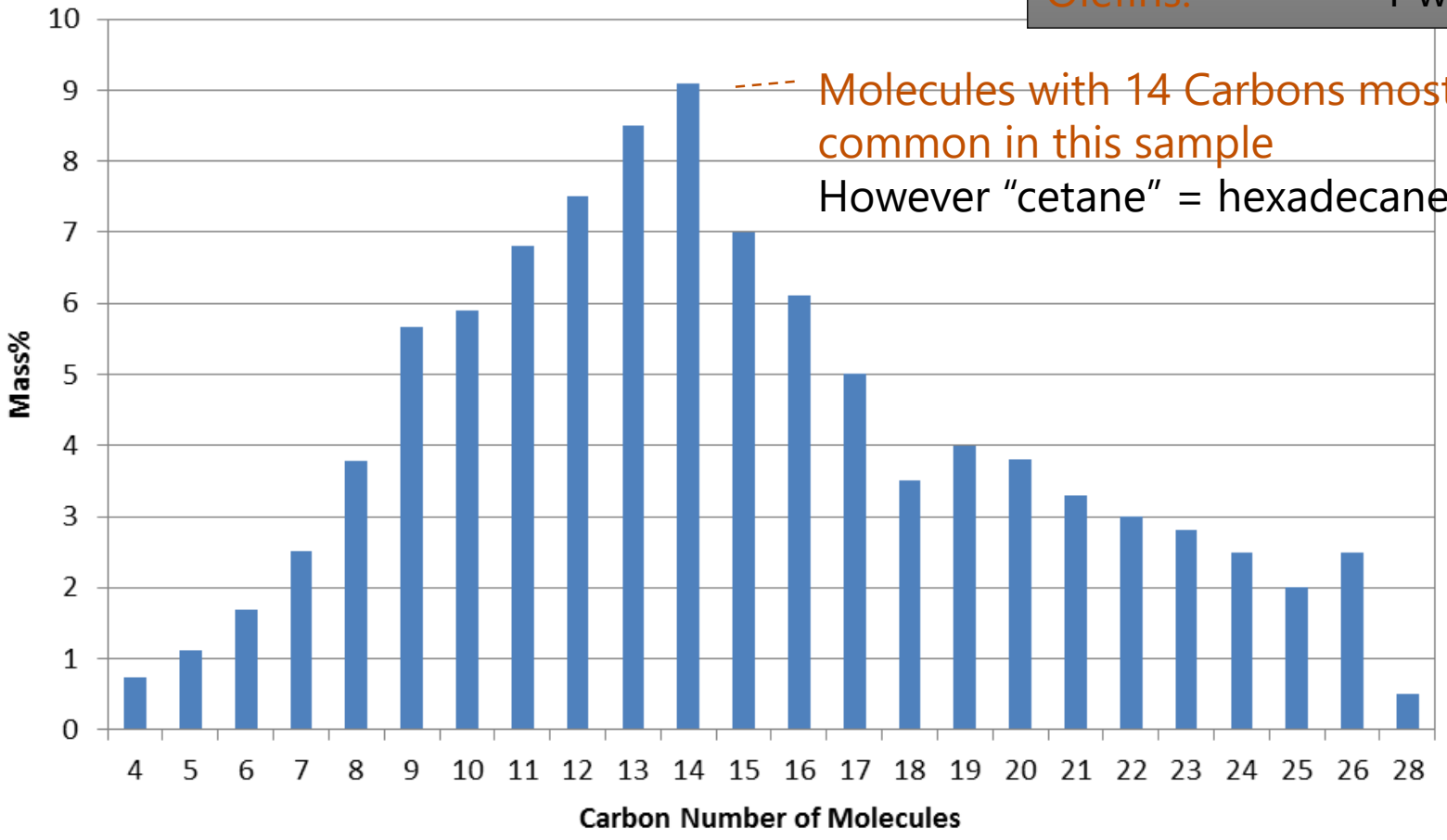
- Many places mandate certain percentages of oxygenates
  - Volatile organic compound (VOC) and CO emissions can be reduced for some older vehicles
    - Oxygenates mostly added for winter-related emissions reduction
    - but can increase NO_x
  - Ethanol, Methanol, n-Butanol, t-Butanol
  - Methyl-Tert-Butyl-Ether (MTBE) – replaced lead, used because oxygenates were mandated by Congress and preferable to Ethanol.
    - Banned in most US States, Very little in Canada.
    - Can get in drinking water, effects unknown, maybe cancer.
- Limits on sulfur, benzenes, aromatics, and olefins
  - These can increase harmful VOC, CO, and toxic emissions
- Renewable fuel standards
  - Some are explicitly ethanol
  - Some are generic to renewable sources

Sources: BP "Fuel Your Mind" seminar, 2009 gasoline module. American Cancer Society, "MTBE". Environment Canada, "Use and Releases of Methyl Tertiary-Butyl Ether (MTBE) in Canada" (2013)

Diesel

- A denser, more viscous blend of hydrocarbons than gasoline
- Typical #2 diesel:

Aromatics:	14 wt%	(benzene, etc)
Naphthalenes:	39 wt%	(cyclic alkanes)
Parrafins:	45 wt%	(branched alkanes)
Olefins:	1 wt%	(alkenes)



---- Molecules with 14 Carbons most common in this sample

However "cetane" = hexadecane = C_{16}

Sources: Biofuels from continuous fast pyrolysis of soybean oil: A pilot plant study, Bioresource Technology, Volume 100, Issue 24, December 2009, Pages 6570–6577
Category data from Sjogren et al. Fuel 74:7:983-989 (1995)

McMaster University ENGINEERING

McMaster Advanced

Other Issues

- Cetane Rating measures ignition delay of diesel
  - Shorter ignition is better
  - Typical truck diesel is 40 cetane, premium is 47-50 cetane
- Emissions are different than gasoline
  - NO_x is significant, regulations gradually improving
  - CO and VOC are insignificant
- Typical diesel fuels:
  - No. 1 Diesel (45 cetane, similar to Kerosene, Jet A. "winter diesel")
  - No. 2 Diesel (most common type. 40-45 cetane. "summer diesel")
  - No. 3 Diesel (now defunct)
  - No. 4 Diesel (industrial engines, not for mobile applications)

Sources: BP "Fuel Your Mind" seminar, 2009 diesel module
http://flashoffroad.com/Diesel/DieselFuel/about_diesel_fuel.htm

The People's Car

- US EPA has emissions standards on NOx from diesel engines (some US states and the EU have stricter ones)
  - There are standard tests that must be passed
  - Cars are stationary, driving conditions are simulated (particular speeds, etc).
- Evidence had been mounting in Europe (2014) that the tests probably weren't that good
  - General NOx levels higher than should be
  - Tests on many cars in Europe showing higher emissions in road conditions than in test conditions.
- International Council on Clean Transportation commissioned three studies:
  - One was US based because those vehicles had higher standards and they wanted to show the Europeans that it could be done
  - Also wanted to find correlation between real world driving and the testing method.
  - U West Virginia was able to test three diesel cars, driving from Seattle to LA, about 4000 miles each

Sources: BBC News, Volkswagen: The scandal explained. Oct 7 2015.
Thompson GJ, Carder DK, Besch MC, Thiruvengadam A, Kappanna HK. In-Use Emissions Testing of Light-Duty Diesel Vehicles in the United States. Center for Alternative Fuels, Engines and Emissions, U West Virginia, May 2014.
US EPA. EPA, California Notify Volkswagen of Clean Air Act Violations / Carmaker allegedly used software that circumvents emissions testing for certain air pollutants. Sept 18 (2015)
Bigelow P. West Virginia researcher describes how Volkswagen got caught. Autoblog.com Sept 23 (2015).

The People's Car Pt 2

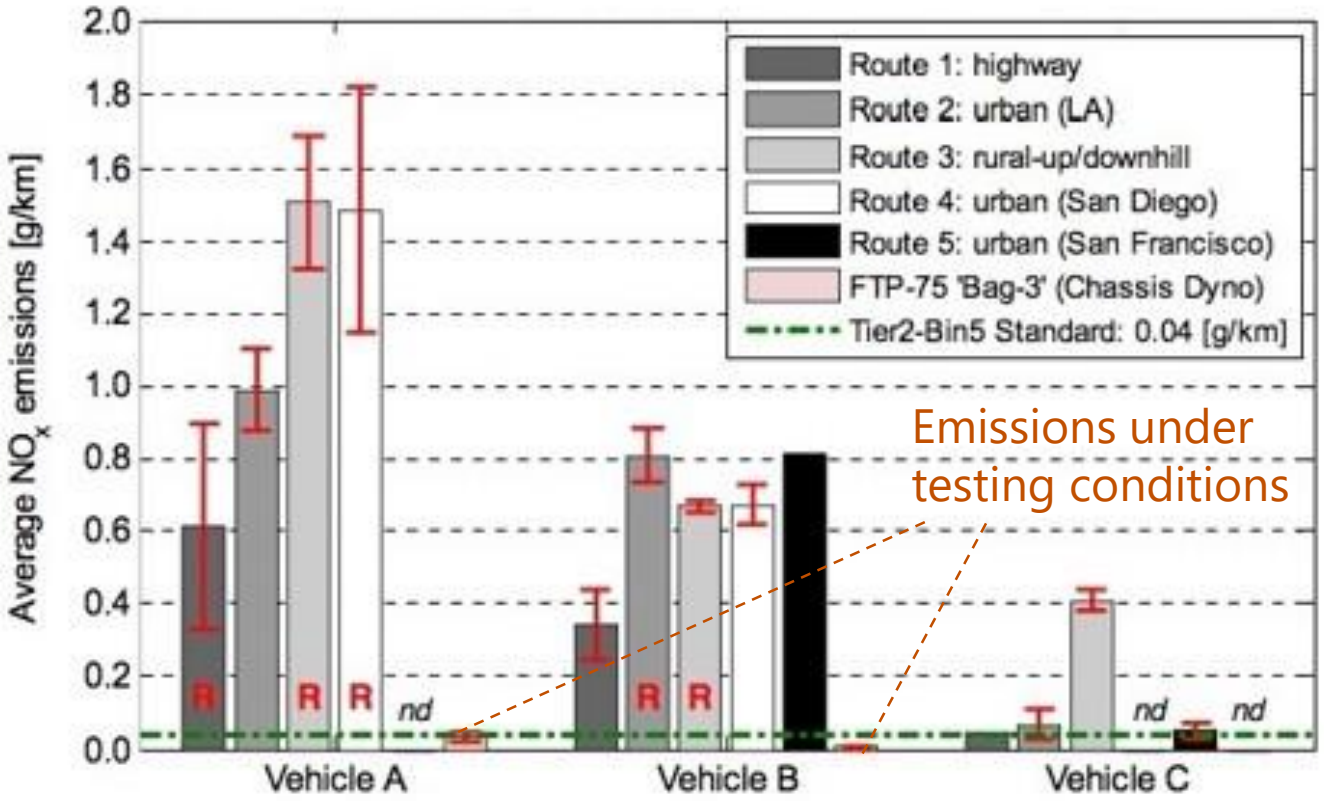


Figure 4.3: Average NO_x emissions of test vehicles over the five test routes compared to US-EPA Tier2-Bin5 emissions standard; repeat test variation intervals are presented as ±1σ; Route 1 for Vehicle A includes rush-hour/non rush-hour driving, '*R*' designates routes including a test with DPF regeneration event, '*nd*' - no data available

McMaster University ENGINEERING

MACC McMaster Advanced Control Consortium

Sources: Thompson GJ, Carder DK, Besch MC, Thiruvengadam A, Kappanna HK. In-Use Emissions Testing of Light-Duty Diesel Vehicles in the United States. Center for Alternative Fuels, Engines and Emissions, U West Virginia, May 2014.

The People's Car Pt 3

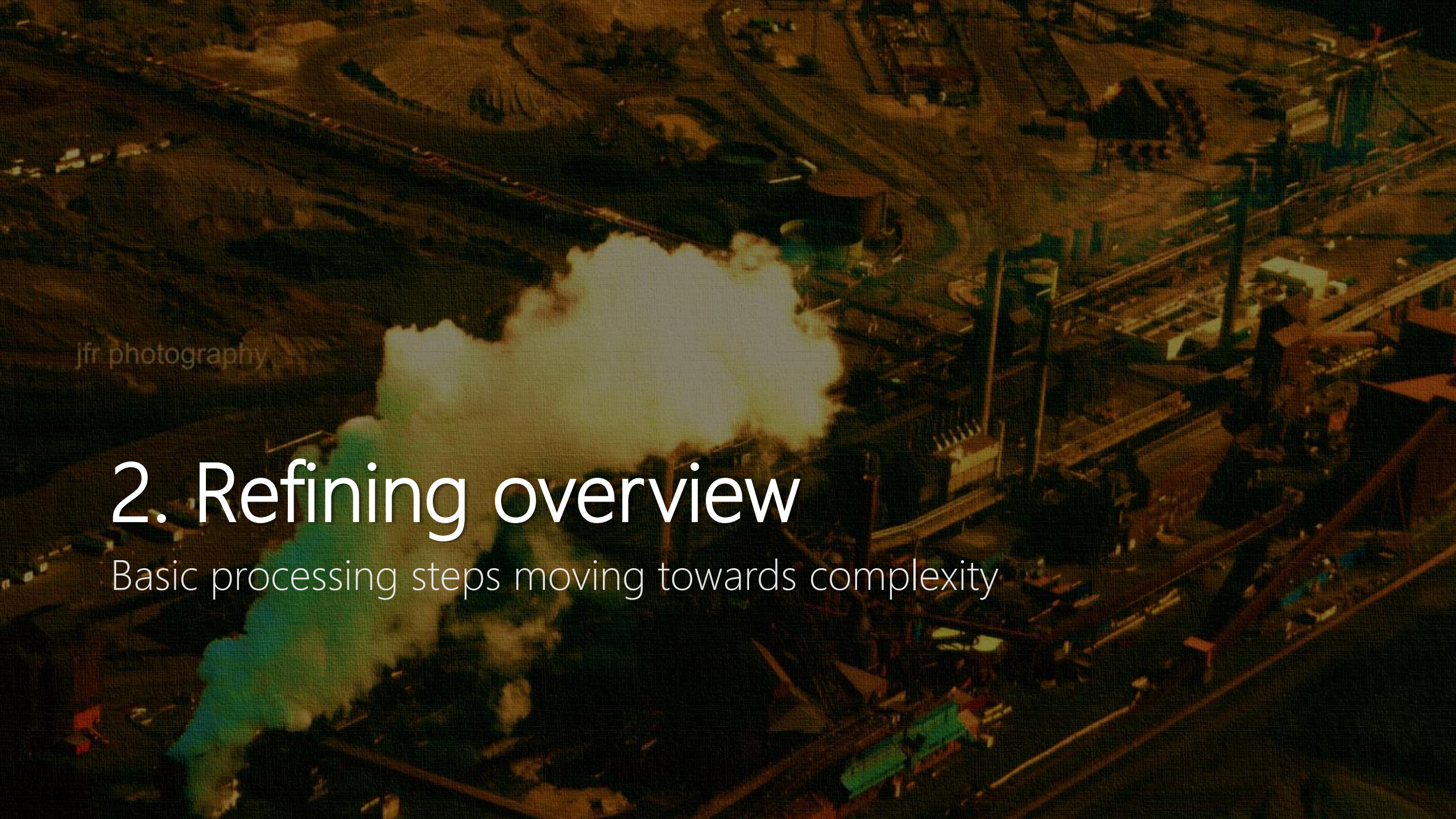
- Results
  - "Vehicle A" – Violated US EPA standards consistently @15-35x limit
  - "Vehicle B" – Violated US EPA standards consistently @5-20x limit
  - "Vehicle C" – Violated US EPA standards only during hills, by 10x
- The researchers were surprised by the first two.
  - Those two vehicles (although never mentioned in the report) were among the best of those in testing conditions and they each had different a NOx reducer technology (*Clue #1*)
    - A had a Lean NOx Trap
    - B & C had urea-based Selective Catalytic Reduction
- The third car results were expected
  - Previous EU data from a great many different cars showed that things got harder to manage when on hills
  - (This is why they wanted a new test.)

The People's Car Pt 4

- The UVW study noted "interestingly" high methane emissions in Vehicles A and B, which was "surprising"
  - Could not suggest an explanation, shouldn't be that much there if the NOx reducers were working even marginally well. (*Clue #2*)
  - The report did not mention the brands… but… only one manufacturer used the Lean NOx Trap. Only later it was revealed:
    - Vehicle A: VW Jetta Vehicle B: VW Passat Vehicle C: BMW X5
- Sept 2015: EPA makes formal finding against VW
  - Couldn't explain it either, but demanded a fix anyway.
  - VW later admitted it had a "defeat device".

The defeat device explained

- The Jetta had a Lean Nox Trap (LNT), cheaper. Two stage:
  - Stage 1: Trap mode, where a catalyst "captures" NOx on surface
  - Stage 2: Release mode, when the catalyst is full.
    - Engine now does not burn all the fuel. The extra fuel passes to catalyst
    - Extra fuel reacts with NOx to make N_2, CO2, etc.
    - Bad for fuel economy and performance
  - The "defeat device" was the embedded software code that only ran Stage 2 when the steering wheel wasn't turning but the wheels were. (testing conditions)
    - Stayed in Stage 1 during normal use
    - Once catalyst bed filled up (relatively soon after), all NOx from engine emitted directly with no filter whatsoever
- For the Passat, it had the urea scrubber but only used it during tests

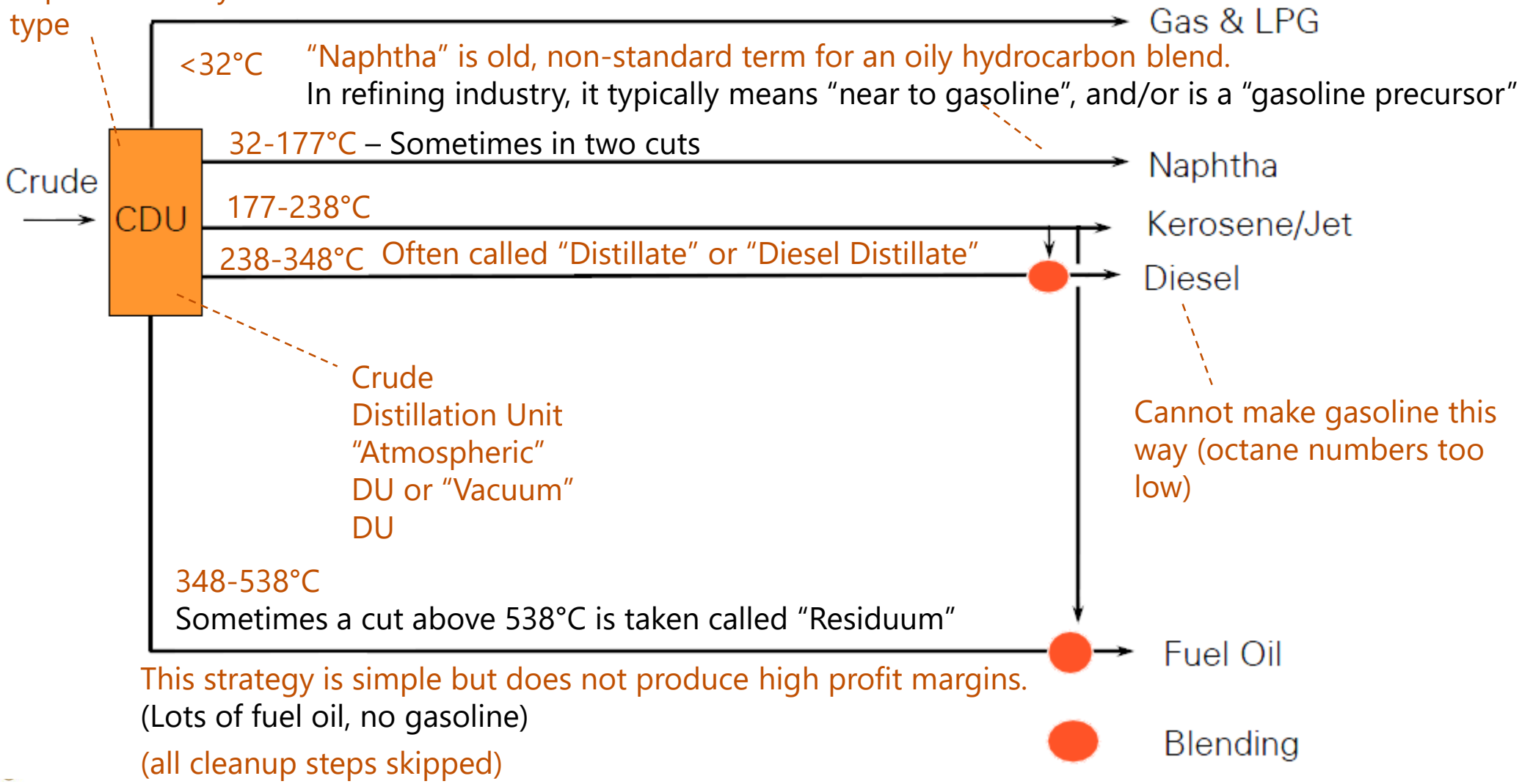


2. Refining overview

Basic processing steps moving towards complexity

"Straight Run" or "Topping"

The distribution of the cuts depends heavily on the crude type



"Naphtha" is old, non-standard term for an oily hydrocarbon blend.
In refining industry, it typically means "near to gasoline", and/or is a "gasoline precursor"

Often called "Distillate" or "Diesel Distillate"

Crude Distillation Unit "Atmospheric" DU or "Vacuum" DU

Cannot make gasoline this way (octane numbers too low)

Sometimes a cut above 538°C is taken called "Residuum"

This strategy is simple but does not produce high profit margins.
(Lots of fuel oil, no gasoline)
(all cleanup steps skipped)

Sources: BP "Fuel Y
Mind" seminar, 20(
Reforming module
Ghosh 2009 – Chap

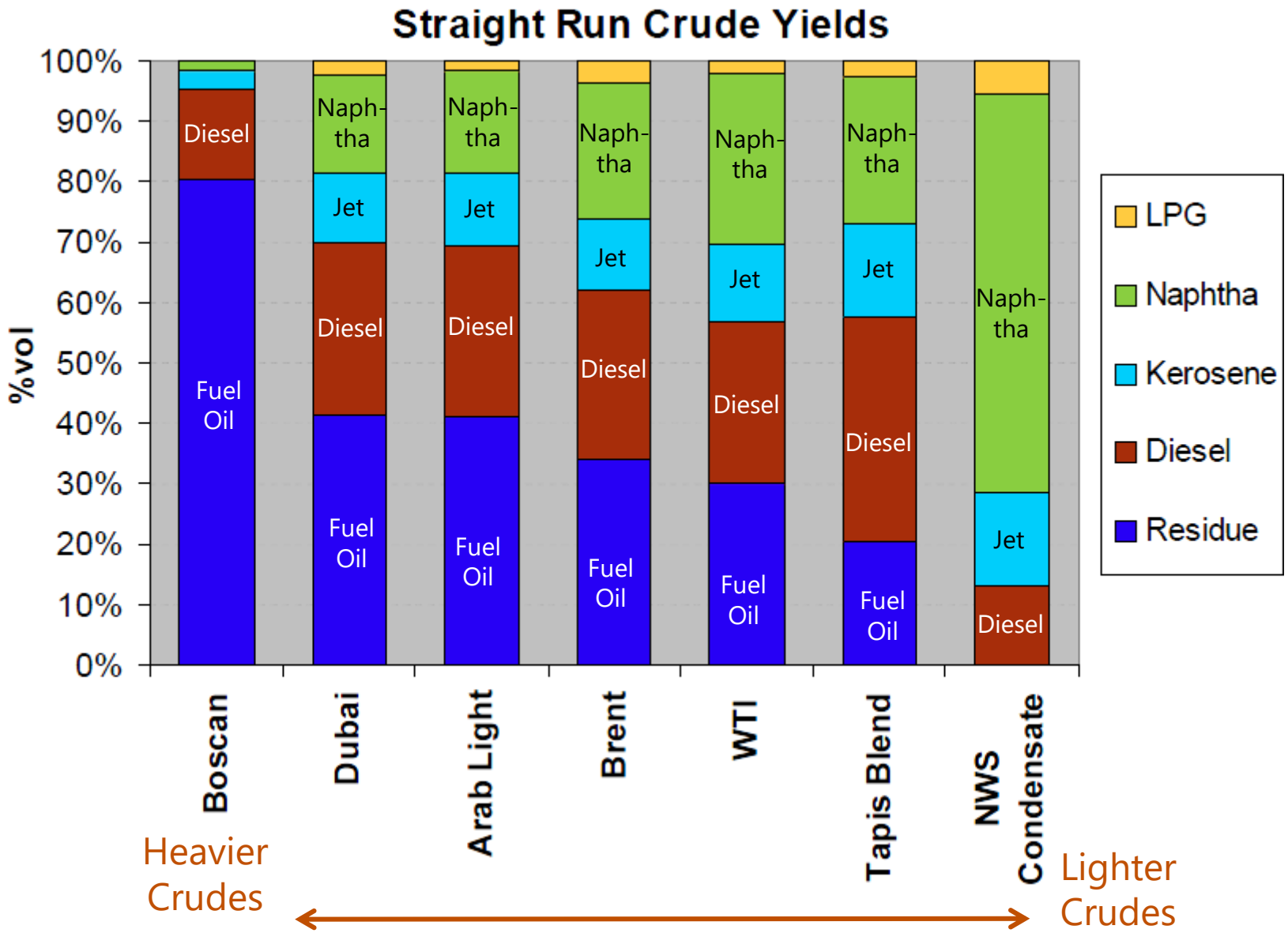
McMast
University
ENGINEERING

Crude Distillation Units

- At a BP facility

Sources: BP "Fuel Your Mind" seminar, 2009 Reforming module

Different Crudes give Different Yields



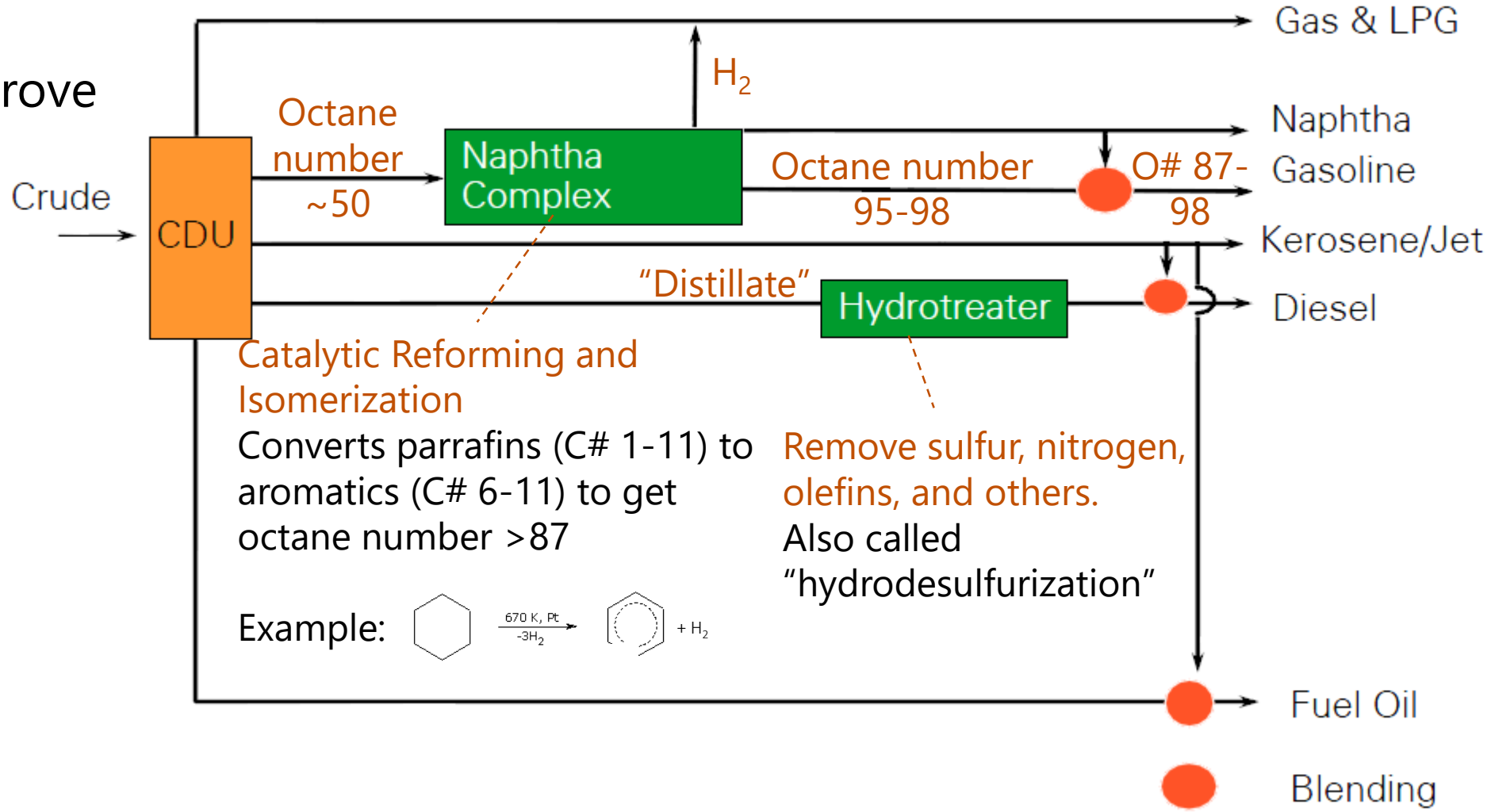
Sources: BP "Fuel Your Mind" seminar, 2009 Reforming module.

McMaster University ENGINEERING

MACC McMaster Advanced Control Consortium

"Hydroskimming" or "Topping & Reforming"

- Now we can get gasoline
- Clean up and improve the quality of the diesel

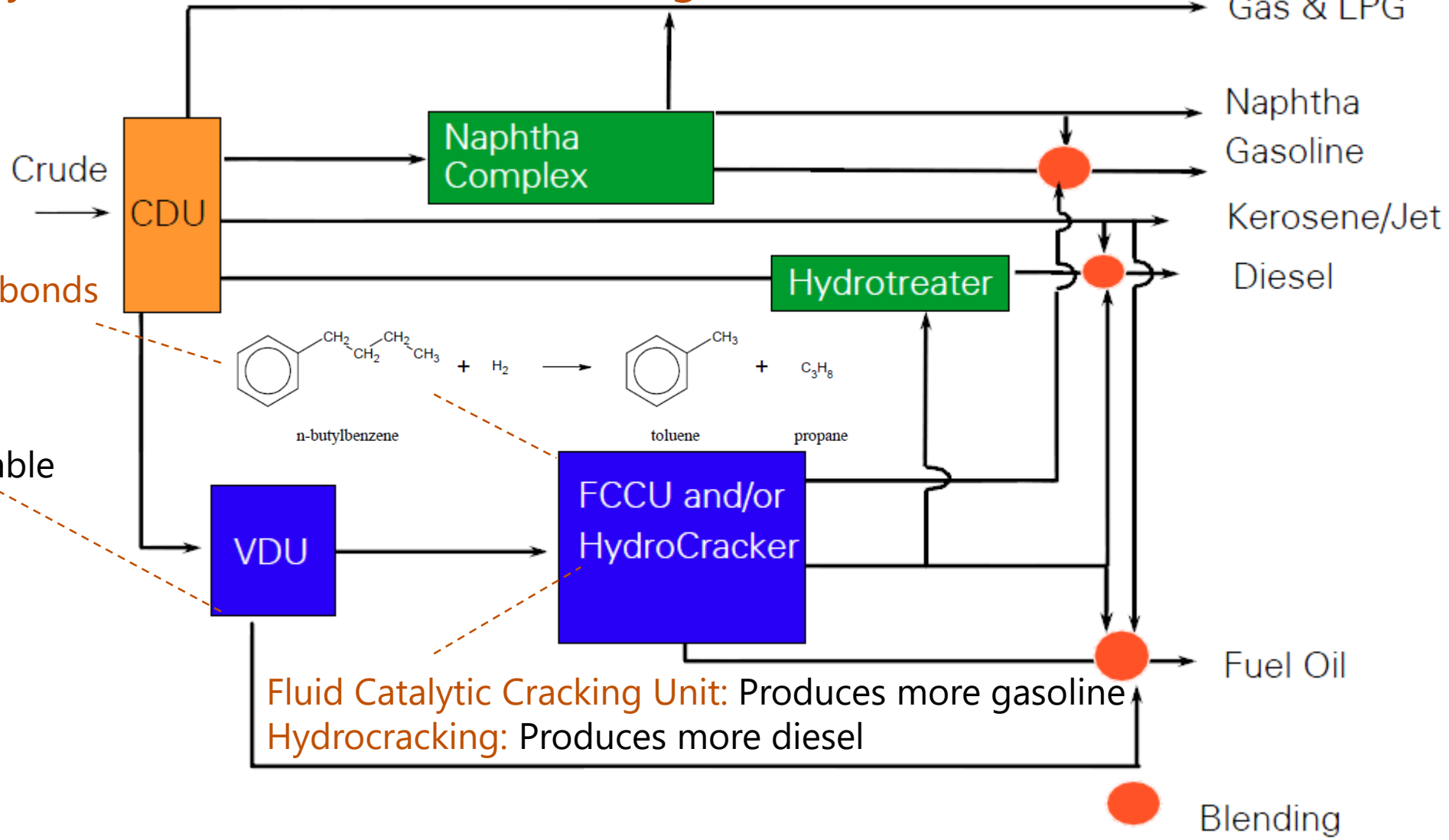


Sources: BP "Fuel Your Mind" seminar, 2009 Reforming module
Ghosh 2009 – Chapter 8

McMaster University ENGINEERING
MACC McMaster Advanced Control Consortium

"Cracking" or "Partial Upgrading"

Converts heavier hydrocarbons to more diesel or gasoline



Cracking: break C-C bonds using H_2. Example:

Vacuum Distillation Unit
Split into more cuts suitable for cracking

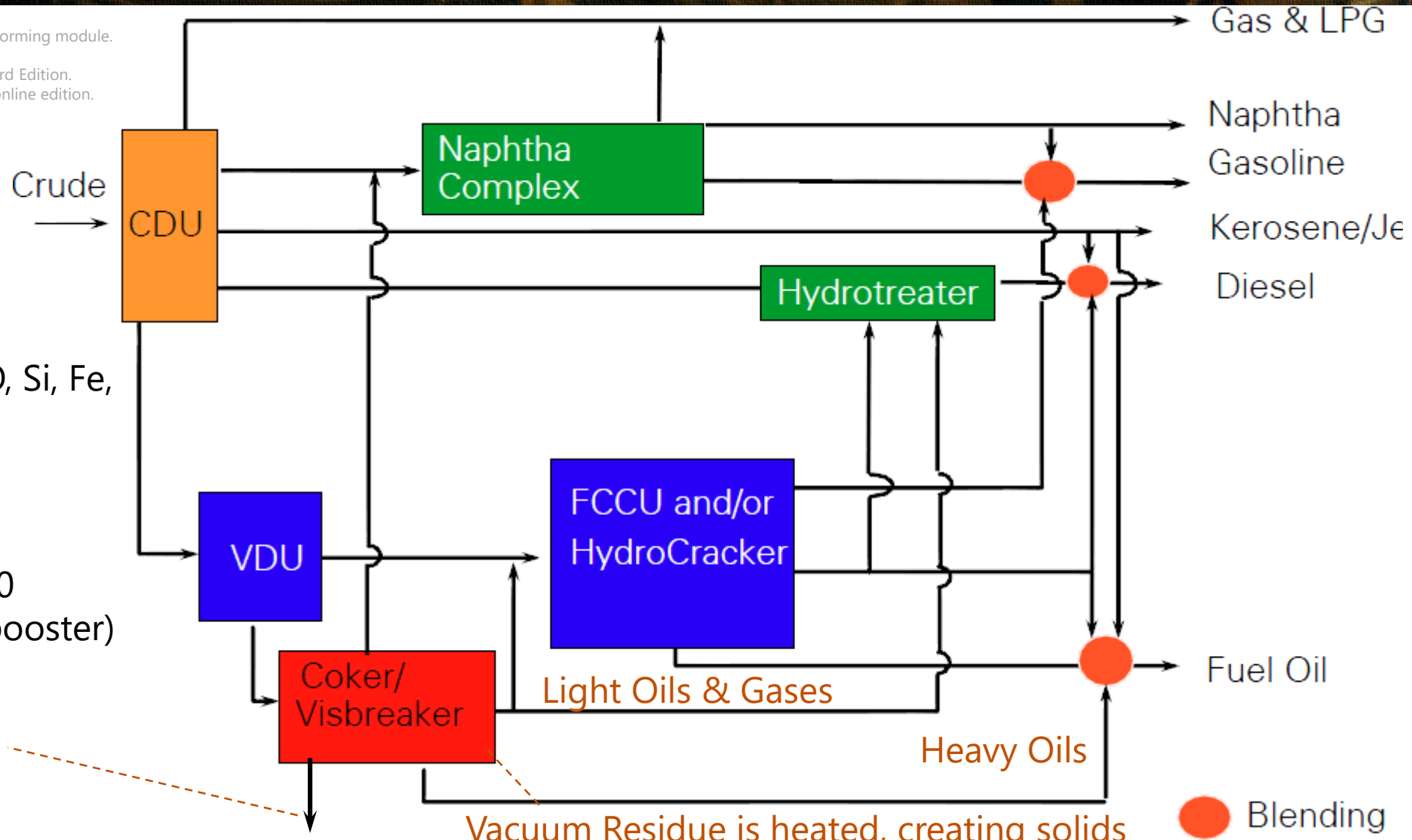
Fluid Catalytic Cracking Unit: Produces more gasoline
Hydrocracking: Produces more diesel

Sources: BP "Fuel Your Mind" seminar, 2009 Reforming module. See also Ghosh 2009 – Chapter 8
Robinson PR, Dolbear GE. Hydrotreating and hydrocracking fundamentals. In : Practical Advances in Petroleum Processing, Hsu CH, Robinson PR (Eds), Springer-Verlag, New York, Chap 7 (2006).

McMaster University ENGINEERING
MACC McMaster Advanced Control Consortium

"Coking" or "Full Upgrading"

Sources: BP "Fuel Your Mind" seminar, 2009 Reforming module.
See also Ghosh 2009 – Chapter 8
Handbook of Petroleum Refining Processes, Third Edition.
Chapter 52. Available via McMaster Library in online edition.



Solid Coke

86-99.5% C

Rest: Volatiles, S, H_2O, Si, Fe, Ni

"PetCoke" Uses:

Fuel (14,000 Btu/lb)

→ coal 8,000-14,000

Steel Industry (coal booster)

Aluminum Industry

Gasification

Stockpile as Waste!

Vacuum Residue is heated, creating solids "coke", light oils & gases, and heavy oils.

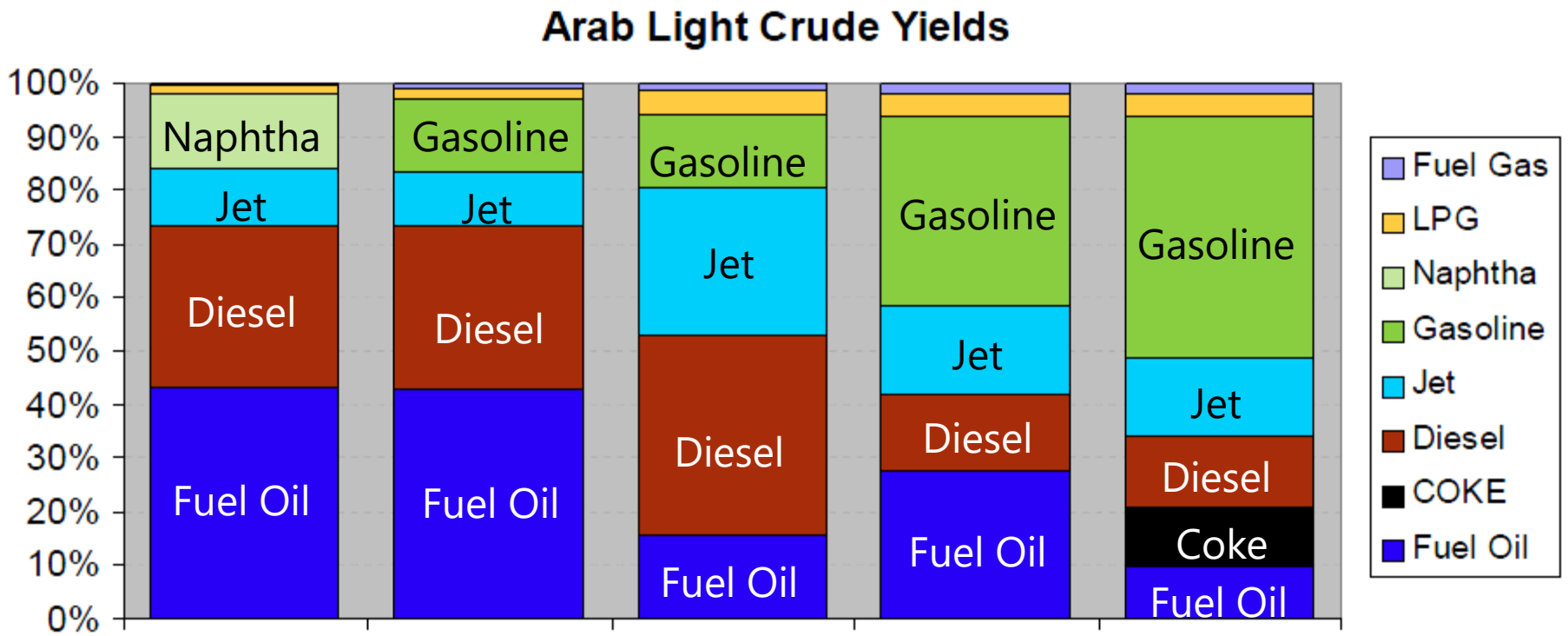
McMaster University ENGINEERING

MACC McMaster Advanced Control Consortium

Product Yields by Process Type

Products for the same crude feed

By volume



Straight Run

Hydro-skimming (Reform Naphtha into Gasoline)

Hydro-cracking (Break heavy cuts into diesel/jet)

Fluid. Catalytic Cracking (Break heavy cuts into gasoline)

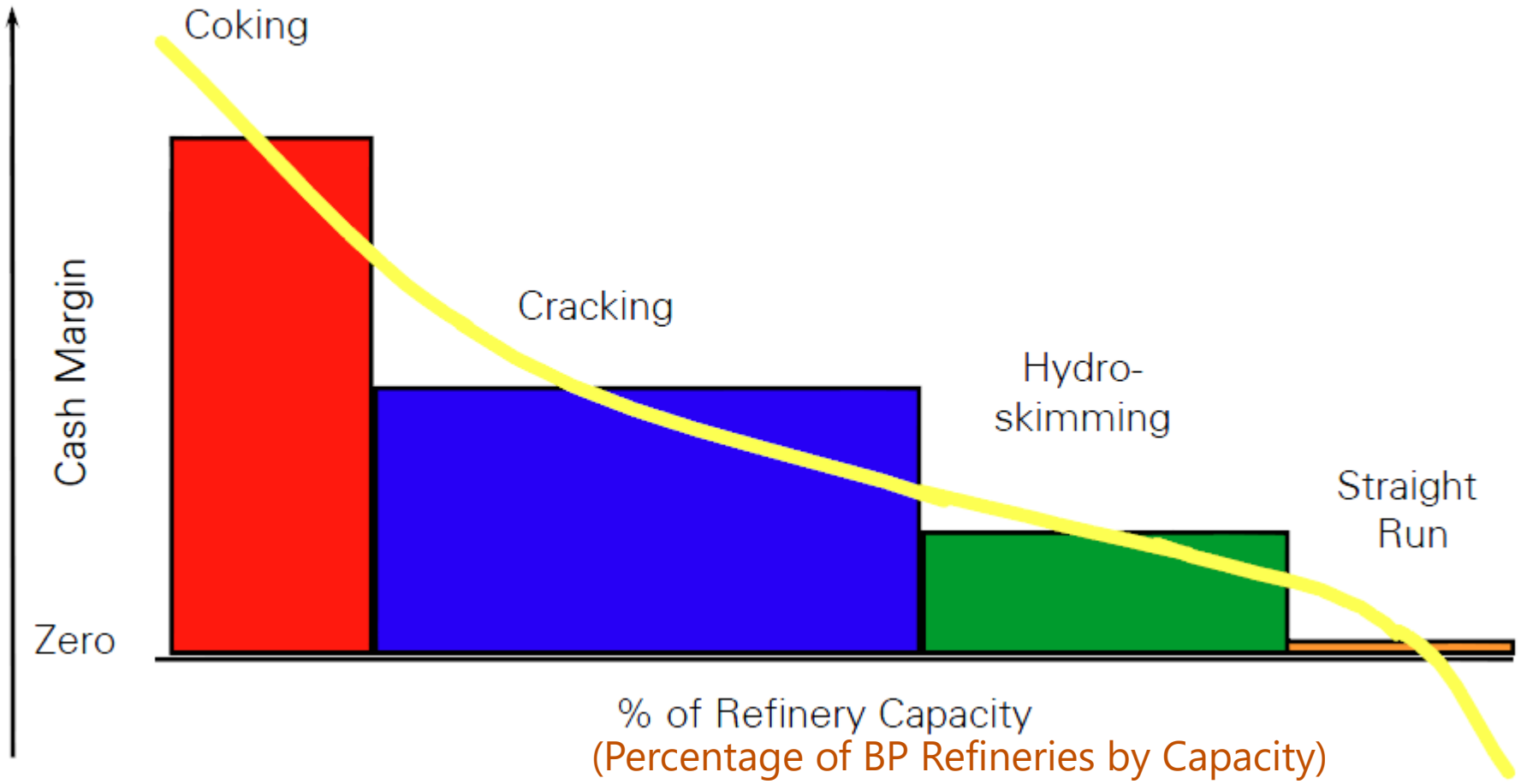
Coking (Convert fuel oils into gasoline)

Sources: BP "Fuel Your Mind" seminar, 2009 Reforming module.

McMaster University ENGINEERING

MACC McMaster Advanced Control Consortium

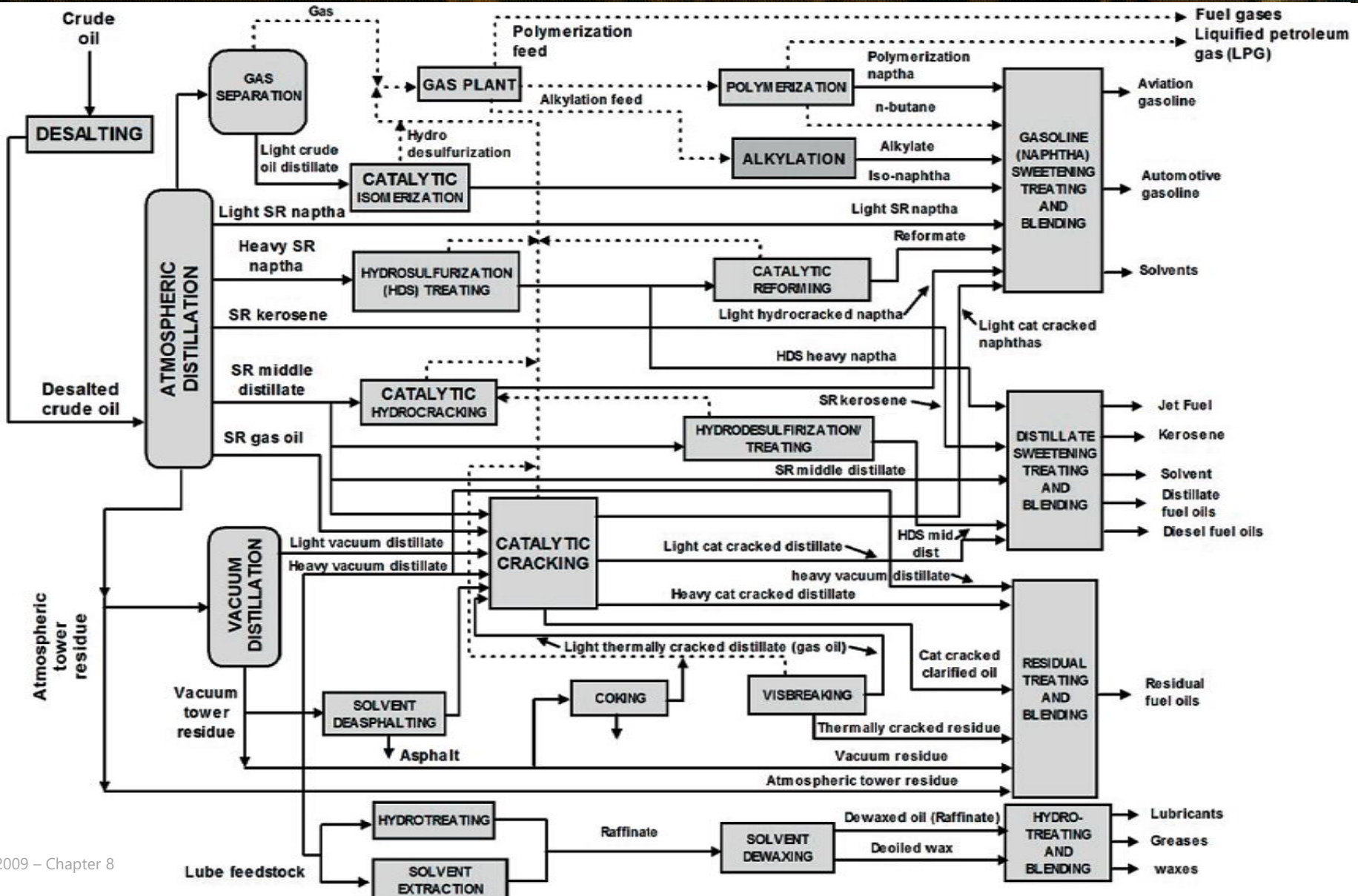
Refinery Types by Popularity



Sources: BP "Fuel Your Mind" seminar, 2009 Reforming module. See also Ghosh 2009 – Chapter 8
Robinson PR, Dolbear GE. Hydrotreating and hydrocracking fundamentals. In : Practical Advances in Petroleum Processing, Hsu CH, Robinson PR (Eds), Springer-Verlag, New York, Chap 7 (2006).

The genesis of our profession

Process for Light Oils



Source: Gosh 2009 – Chapter 8

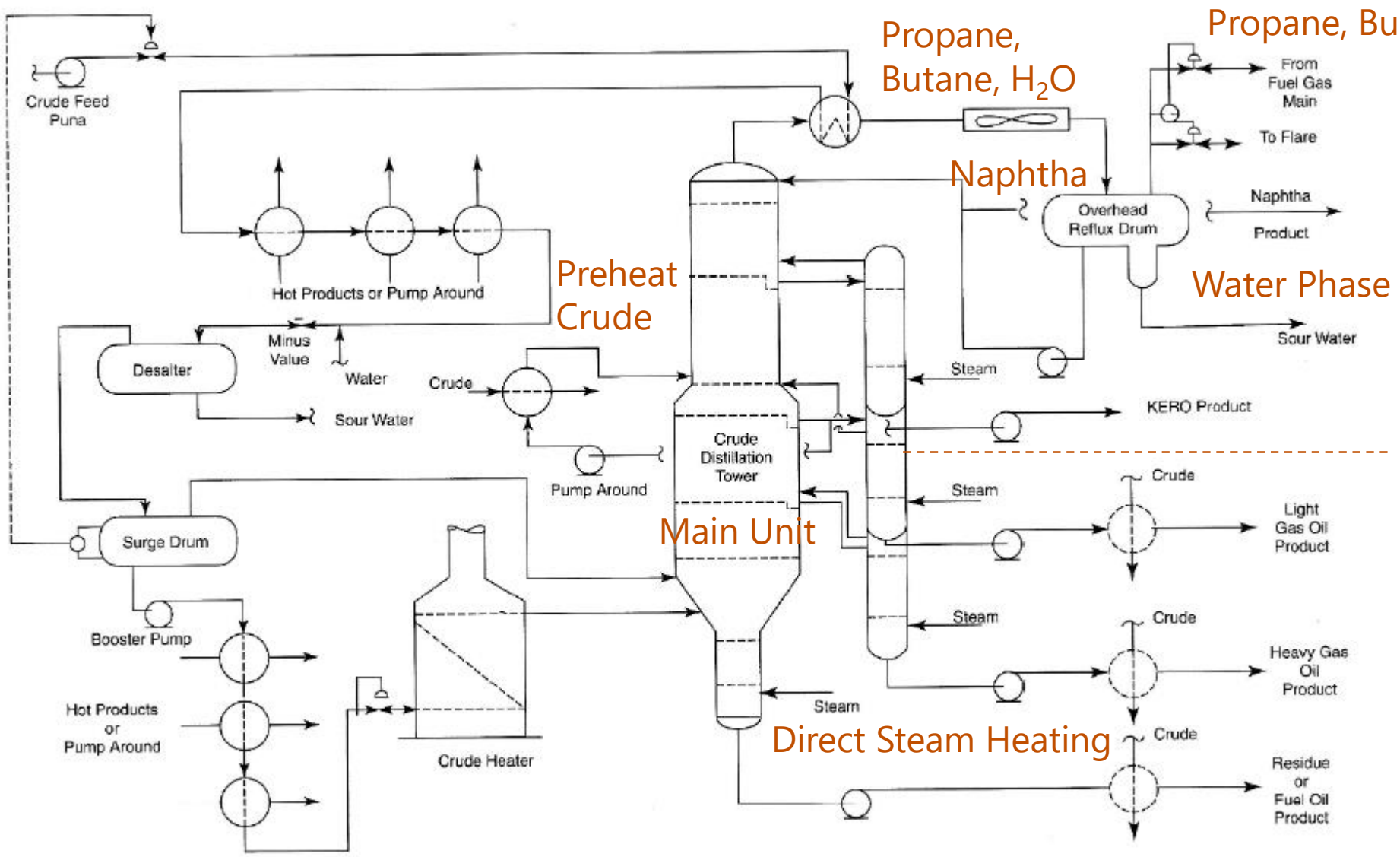
McMaster University ENGINEERING

MACC McMaster Advanced Control Consortium

3. A CLOSER LOOK

Key steps in the refining process

Crude Distillation Unit



Side column used for extra heating and heat integration.

Direct steam heating

Sources: Ghosh 2009 – Chapter 8

Catalytic Reforming

Four stages of reactors (UOP Design)
Stacked vertically for catalyst flow
Parrafins → Naphthenes + H_2
Naphthenes → Aromatics + H_2
Aromatics + H_2 → Lighter Aromatics

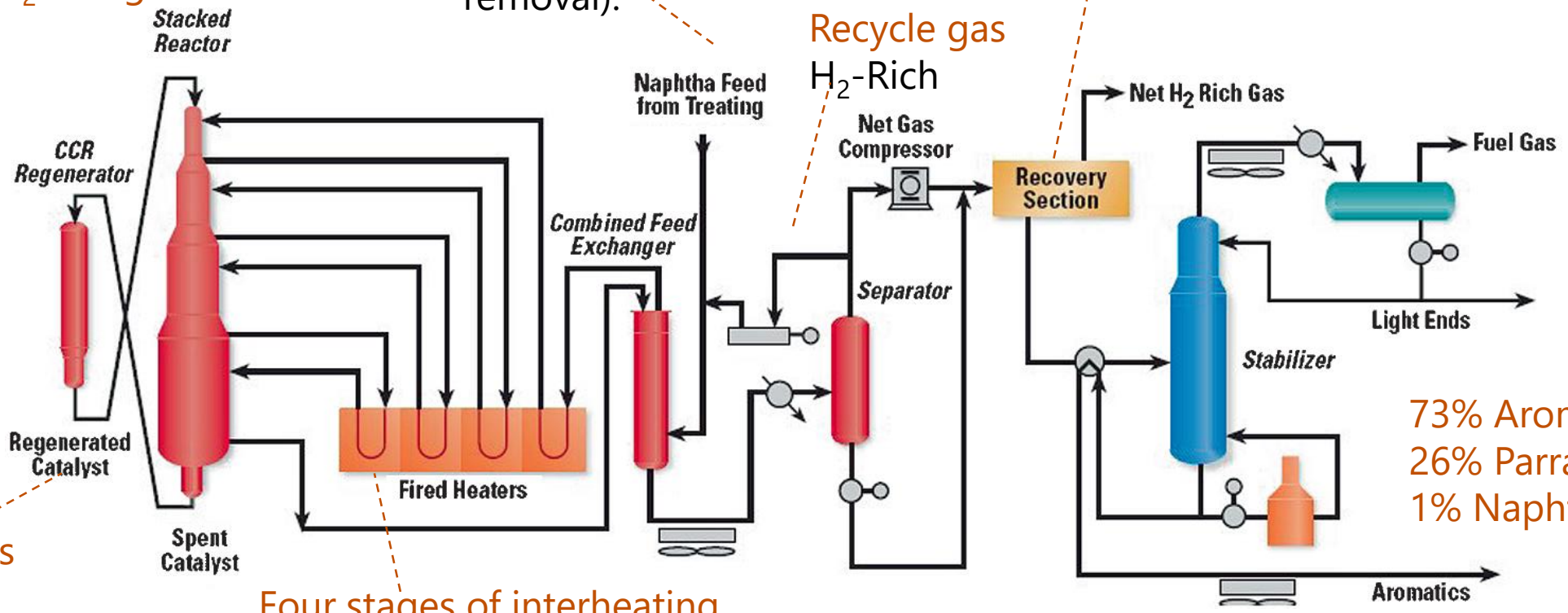
Naphtha after hydrotreating
(sulfur, nitrogen, & olefin removal).

14% Aromatics
55% Parrafins
31% Naphthenes

Separate gases from light & heavy oils

Sources: Ghosh 2009 – Chapter 8

Recycle gas
H_2-Rich



73% Aromatics
26% Parrafins
1% Naphthenes

Catalyst loops
Gravity flow

Four stages of interheating, ~500C at each outlet
Reforming reactions are endothermic

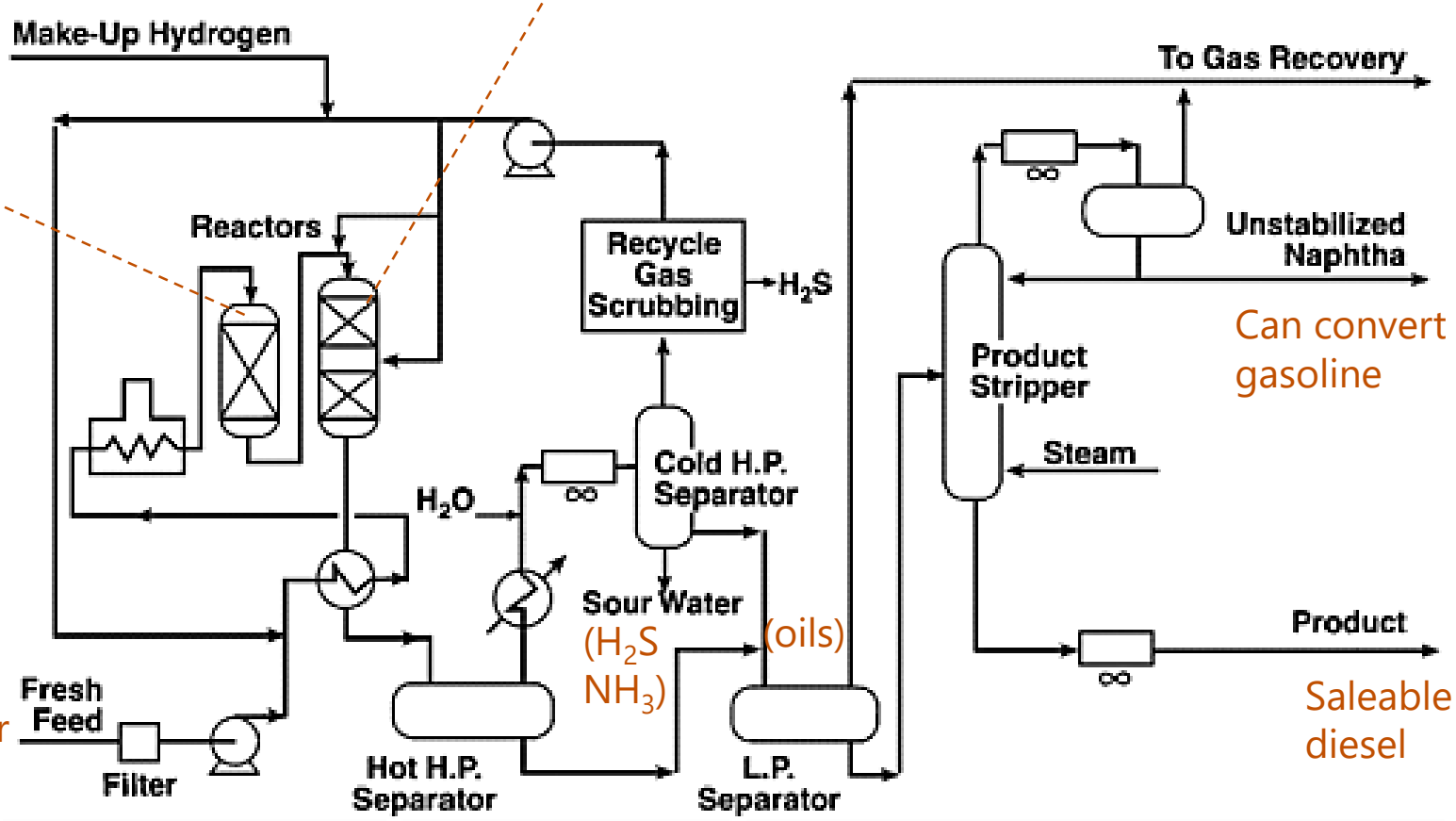
McMaster University ENGINEERING
MACC McMaster Advanced Control Consortium

Hydrotreating

Chevron's Variant of Hydrotreating

Multiple reactor beds (Exothermic)
Optional depending on space and specific final blends
Recycle gas is coolant at intermediate injection points

Liquid Phase Reactions
H_2 + S compounds → H_2S
H_2 + N compounds → NH_3
Also Ni and V converted



Can convert to gasoline

Sour Water (H_2S NH_3)

(oils)

Naphtha, Middles, or Heavy Oils

Saleable diesel

(high pressure process)

H2, H2S recovery & Rough oil split

(drop to atmospheric pressure)

Sources: Handbook of Petroleum Refining Processes, 3rd Ed,

McMaster University ENGINEERING

MACC McMaster Advanced Control Consortium

Fluid Catalytic Cracking

UOP FCC Process
Traditional Version

Flue gas has calorific value 700-780°C
Also has SO_X, NO_X, … needs treatment

Burn catalyst with air
Regenerate it

Catalyst is Fluidized by Updraft Feed
Oil is vaporized by hot catalyst
Catalyst recovered by cyclone

Fractionation like others

Further Fractionation to make finer splits

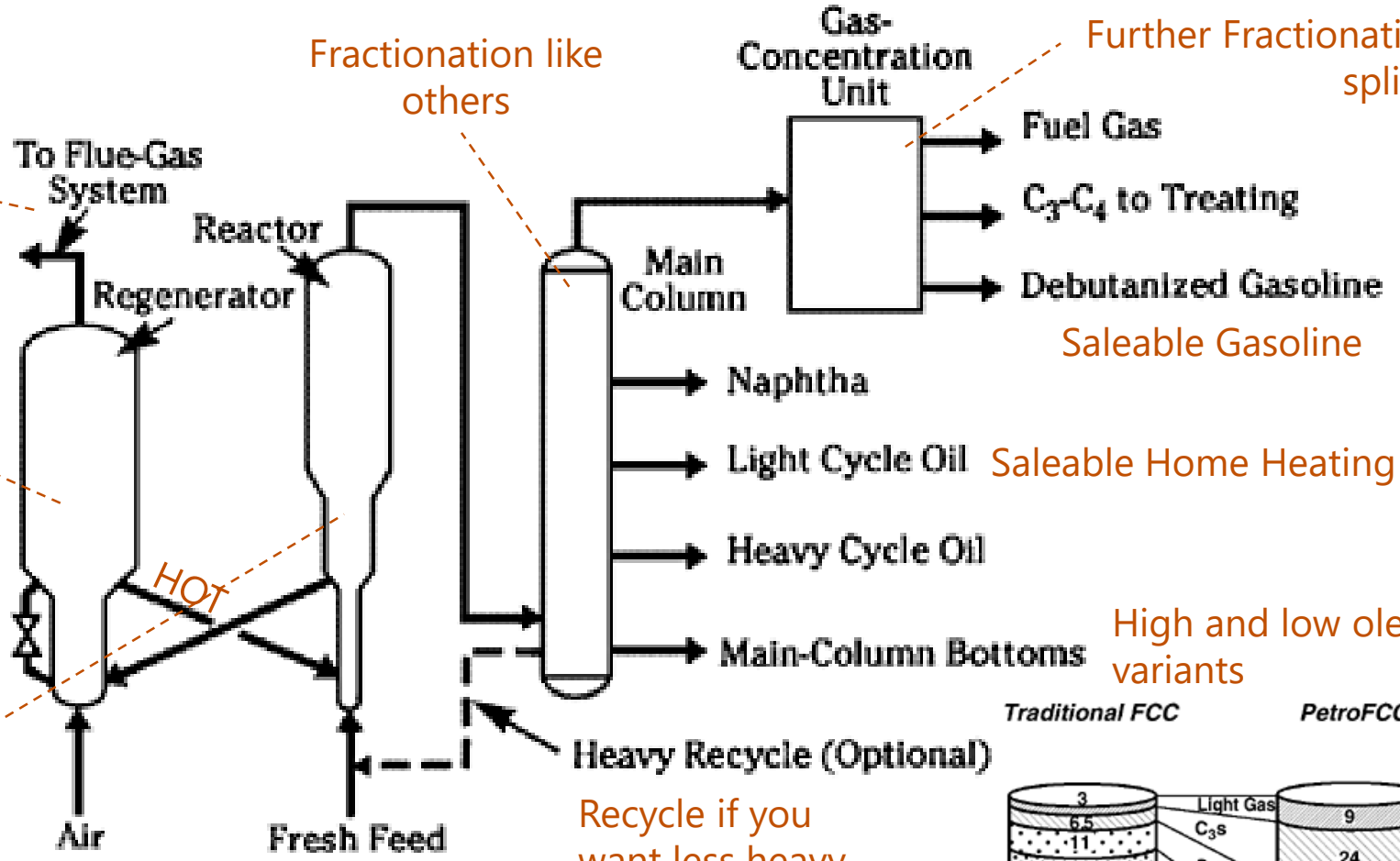
Saleable Gasoline

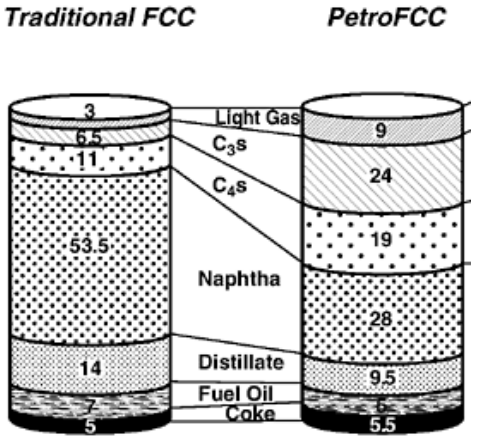
Saleable Home Heating Oil

High and low olefin variants

Recycle if you want less heavy oils

Heavy oils
From CDU or Coker





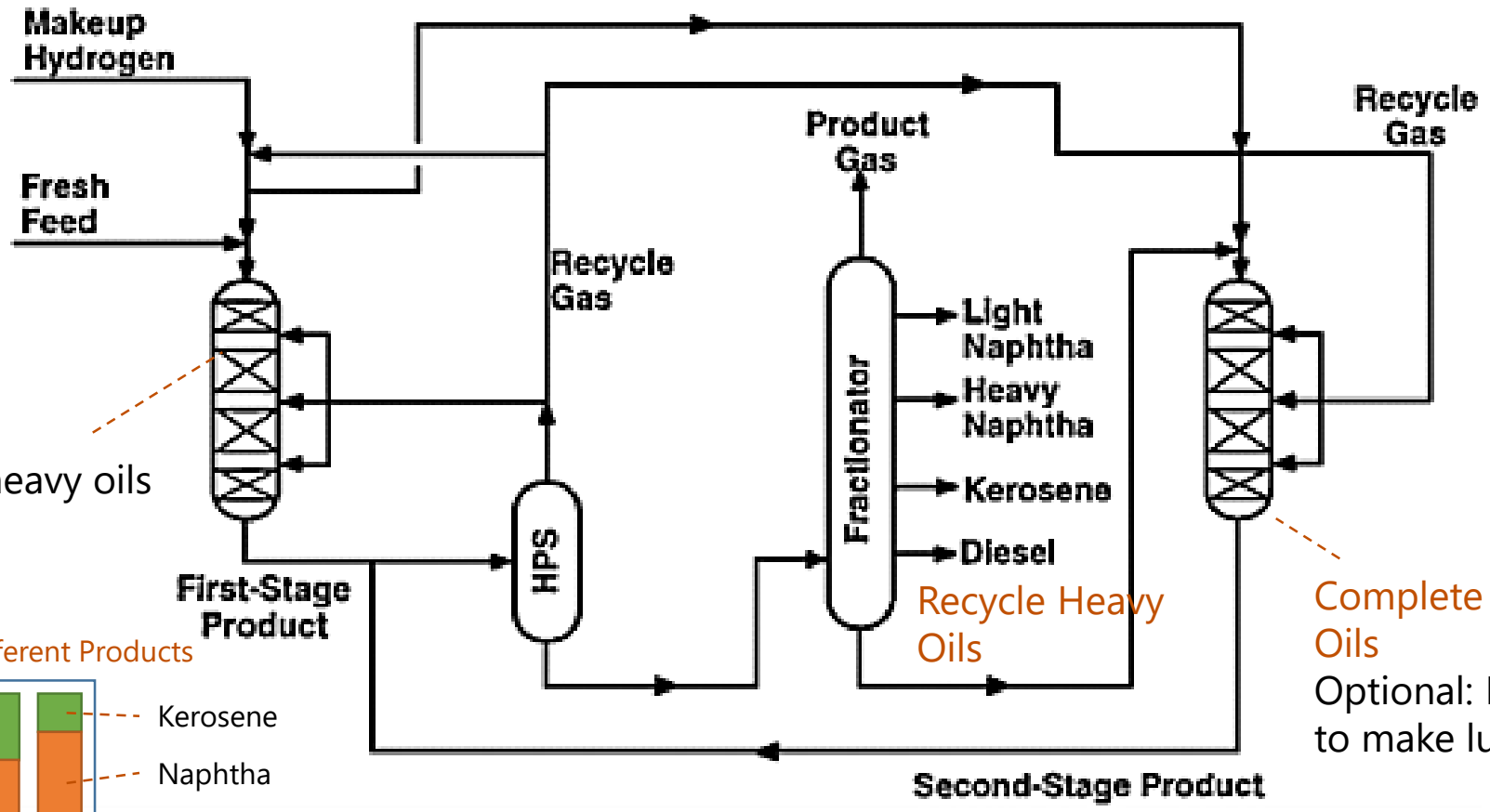
Sources: Handbook of Petroleum Refining Processes, 3rd Ed, Chapter 23

Hydrocracking

Note: Ghosh 2009 Figure 8.25 is wrong!
They are actually showing the UOP version of the one-stage process. Note the text and figure do not correspond.

Heavy oils
From CDU or Coker

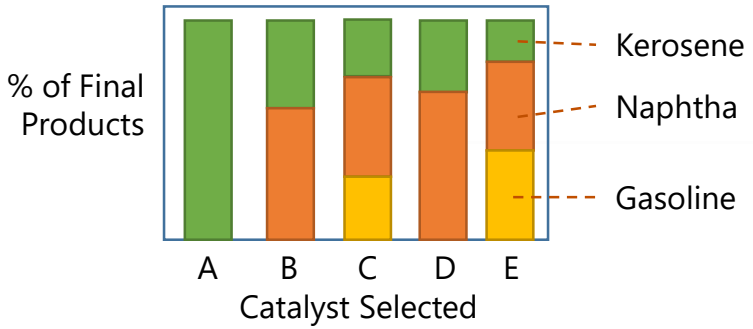
Some Cracking
Higher portion of heavy oils



Recycle Heavy Oils

Complete Cracking of Heaviest Oils
Optional: Don't use if you want to make lubricants

Different Catalysts for Different Products



Chevron's Two-Stage "Isocracking" Process
Nearly 100% conversion of heavy oils

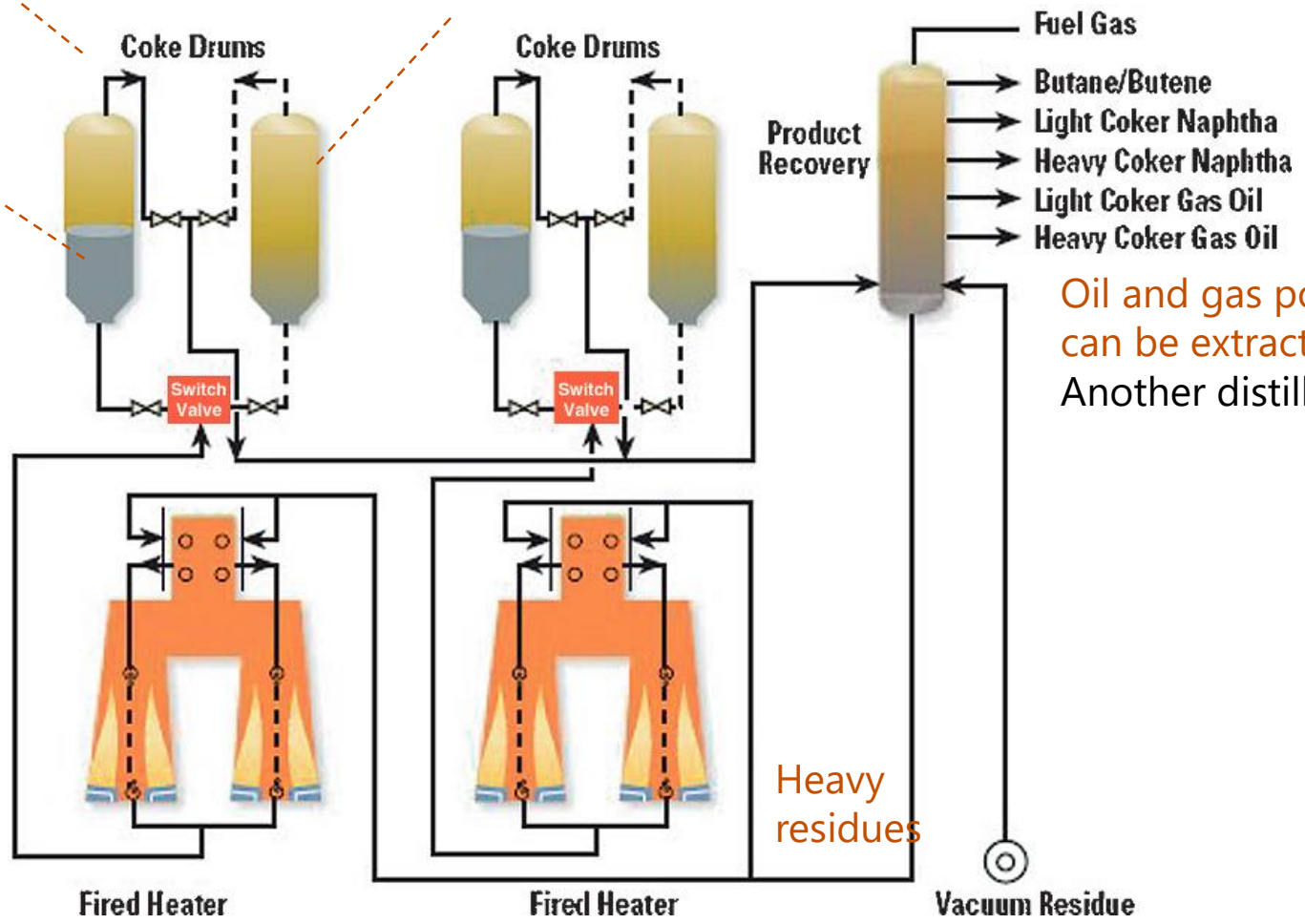
Sources: Handbook of Petroleum Refining Processes, 3rd Ed, Chapter 23

Coking

Two drums in parallel modes
Alternate between collection and discharge

solids in the drum are hard
must be drilled out

Hot solids collect in drums
Gradually crack into small solids and oils

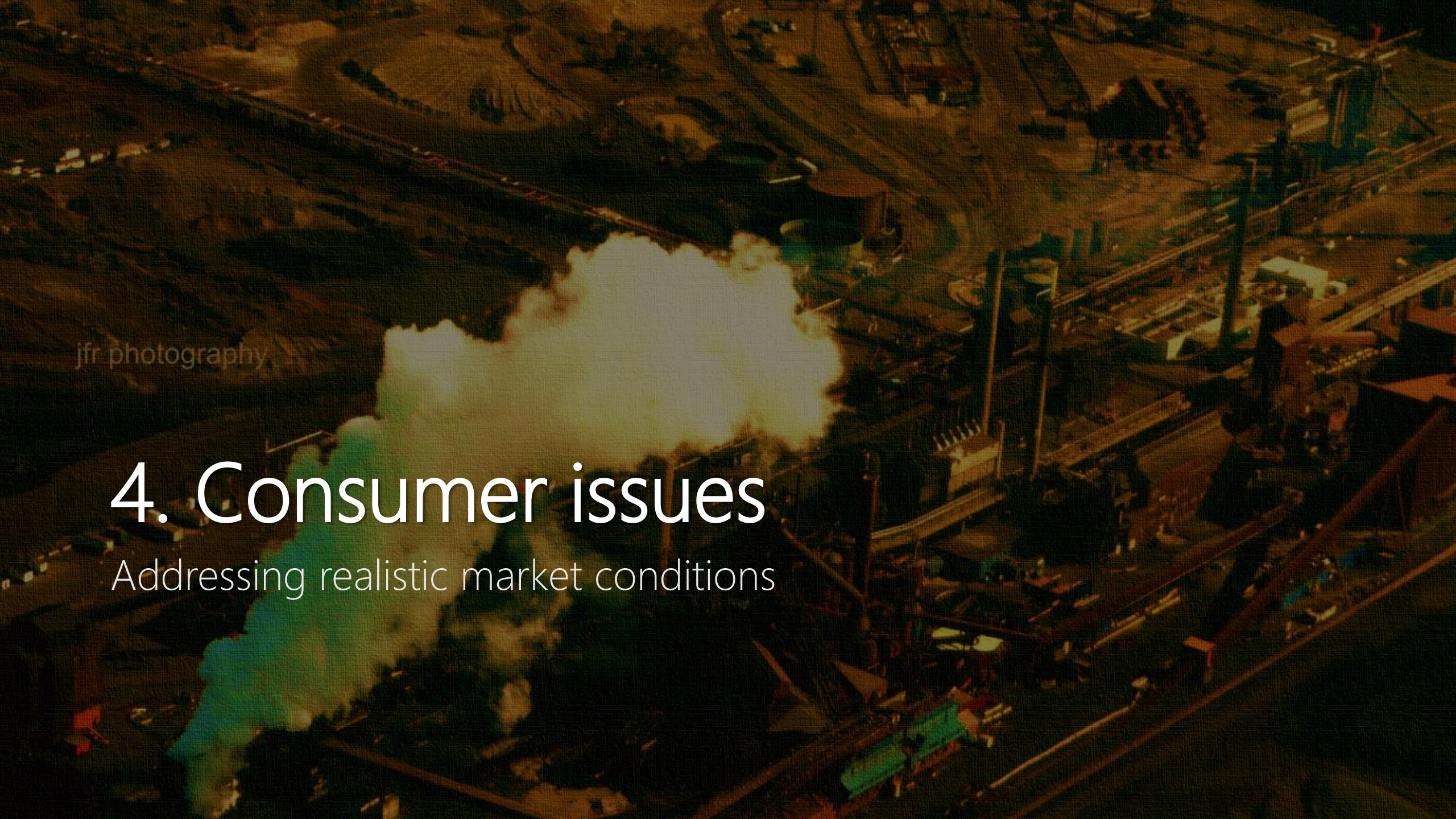


Hot solids rich slurry

Heavy residues

Oil and gas portions that remain can be extracted here
Another distillation unit

Sources: Ghosh 2009 – Chapter 8



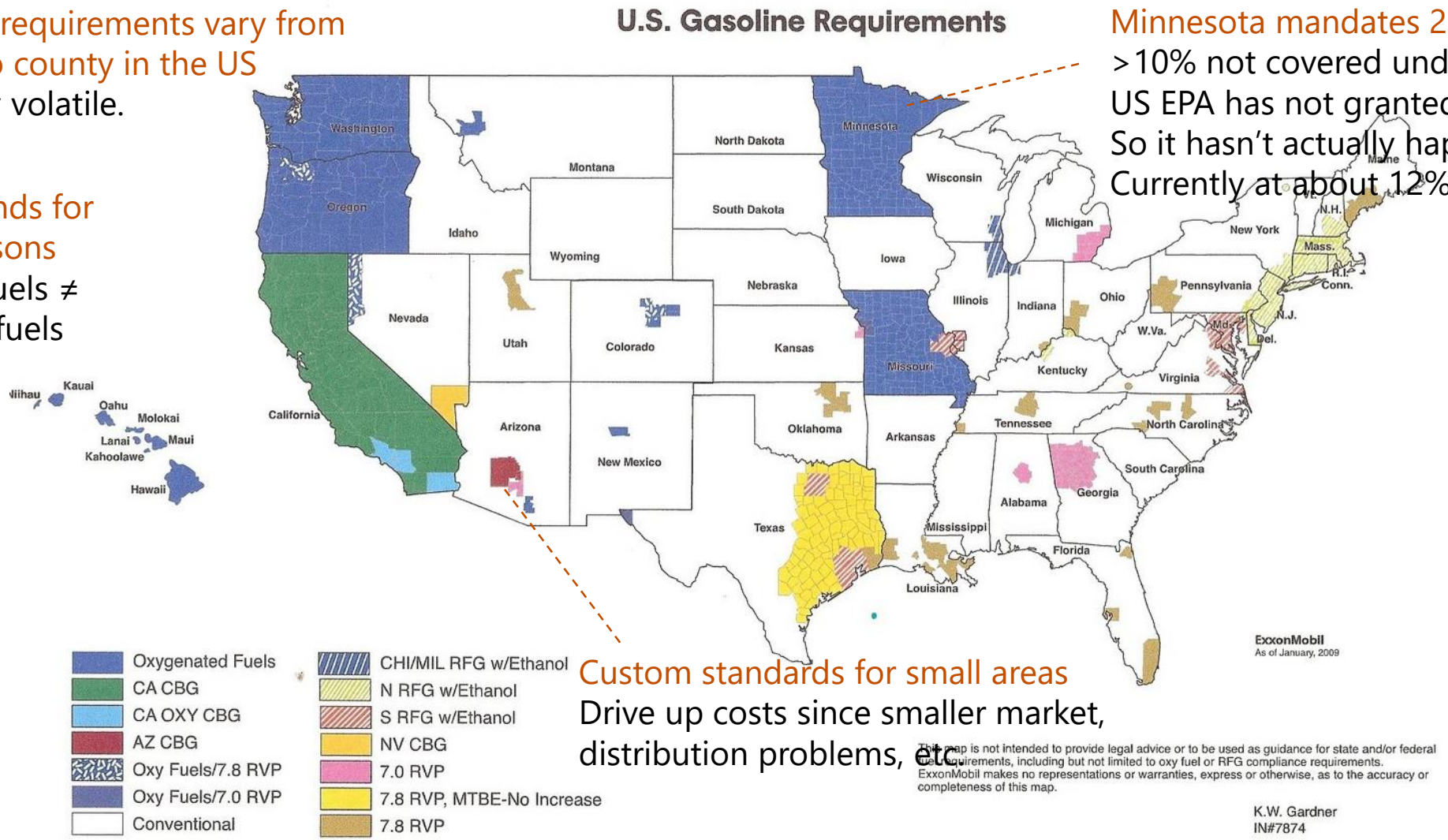
4. Consumer issues

Addressing realistic market conditions

Gasoline Blend Requirements

Gasoline requirements vary from county to county in the US
Politically volatile.

Different blends for different seasons
cold winter fuels ≠ hot summer fuels



Minnesota mandates 20% ethanol
>10% not covered under warrantees
US EPA has not granted approval for E20
So it hasn't actually happened.
Currently at about 12%

Custom standards for small areas
Drive up costs since smaller market, distribution problems, etc

Minnesota Dept of Agriculture, E20 requirement "http://www.mda.state.mn.us/news/government/e20report.aspx".
https://www.cspdailynews.com/fuels/states-hit-ethanol-blending-record

Gasoline Pipelines

Canada tends to export the crude, import the gasoline

Most of the gasoline is piped northward from the Gulf of Mexico region.

Canada does refine, just not as much

Sources: Theodora.com
http://www.theodora.com/pipelines/united_states_pipelines.html

Pipeline & Delivery

- Open secret: refiners put their product in the same pipeline
  - Many refiners and refineries, few pipelines for vast regions
  - Can separate different types in the pipeline in time (plugs)
    - Some interfacial mixing between premium, regular, etc.
    - Pretty good guesses about who made what at what time. But:
  - Conventional gasoline often blended from a mix of refiners
    - Petrocompany pulls "generic" gasoline at terminals, then brands them.
      - Adds own formula of surfactants, anti-knock
      - Add ethanol (can't pipeline ethanol!)
    - Truck to service stations from there
- Some companies own their own exclusive pipelines, but this is limited.

Sources: BP "Fuel Your Mind" seminar, 2009 gasoline module