Refining 101

Dennis Sutton

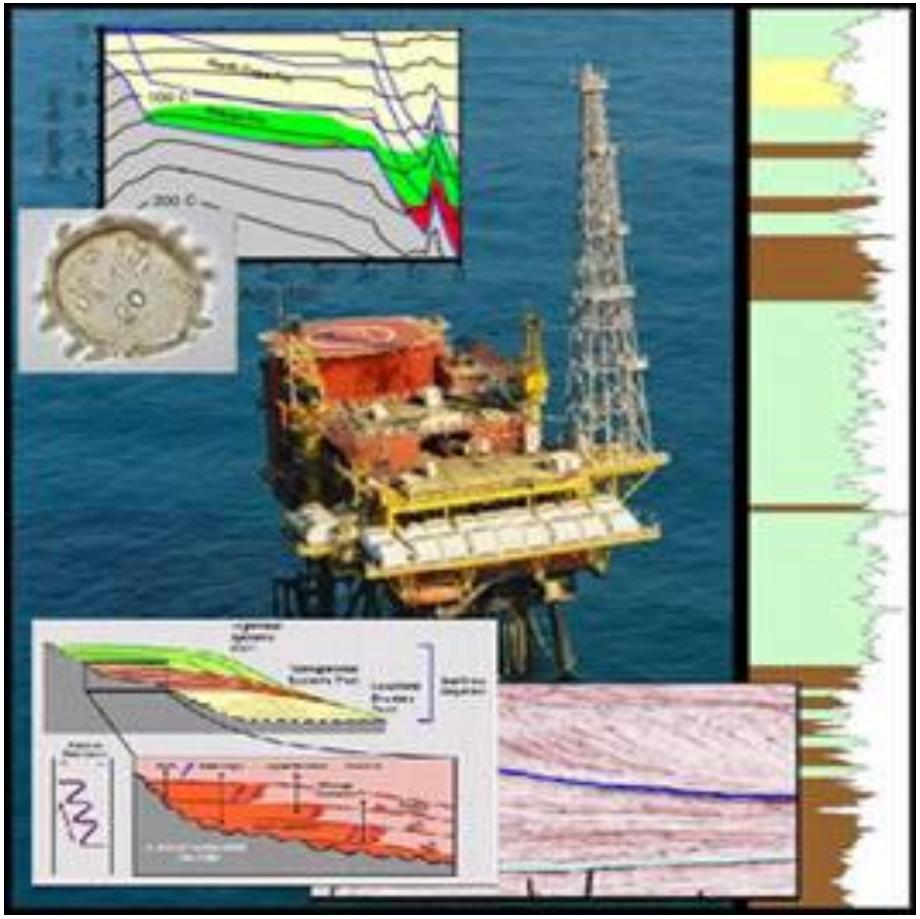
March 2012

Marathon Petroleum Company LP



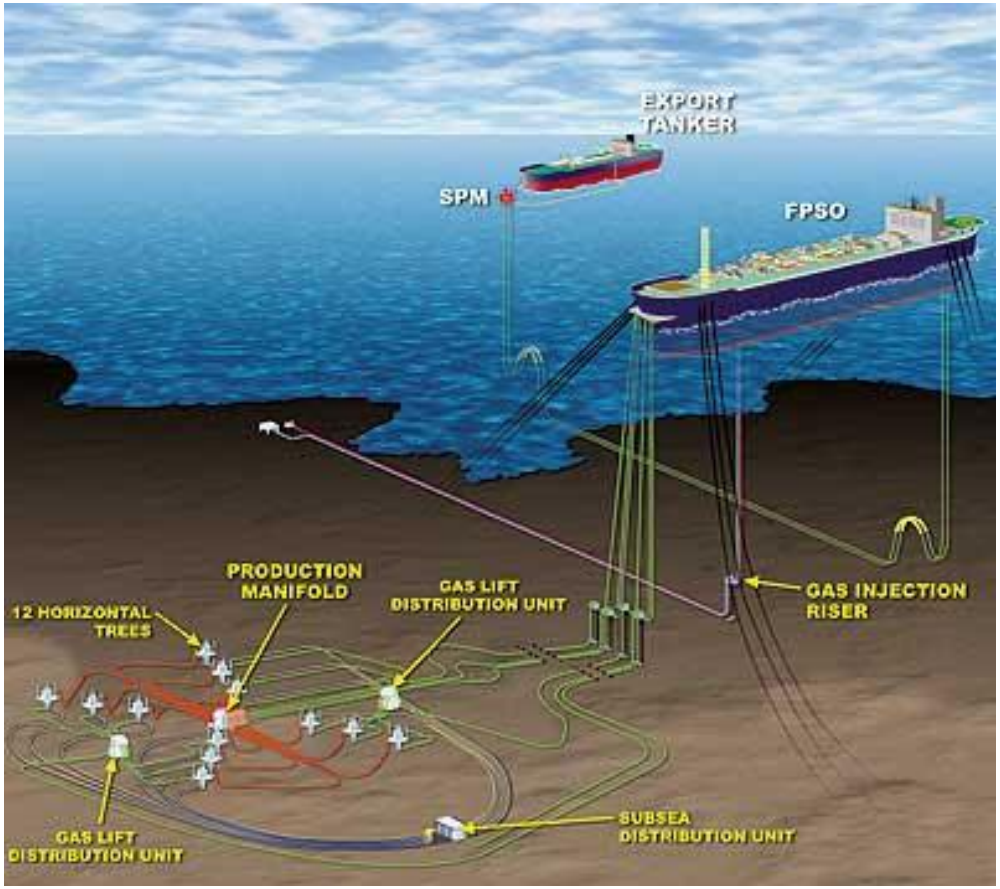
The Petroleum Industry

- Exploration



The Petroleum Industry

- Exploration
- Production & Supply



The Petroleum Industry

- Exploration
- Production & Supply
- REFINING

The Petroleum Industry

- Exploration
- Production & Supply
- REFINING
- Distribution & Marketing

Purpose of Petroleum Refining

Safely, and efficiently transform crude oil and other raw materials into on-spec finished products.

Crude Oil

- To the consuming public, crude oil is the raw material that will ultimately power our vehicles, provide heating, pave our roads, and become the building blocks for many of the plastics we use.

What is Crude Oil?

- Usually naturally occurring
- Not a single compound, but a complex mixture of thousands of compounds
- Wide boiling range
- Mostly hydrocarbons (compounds with carbon and hydrogen) but traces of other compounds are present, such as sulfur, nitrogen, oxygen, and metals

What is Crude Oil?

- Usually naturally occurring- but what about synthetic crude?

What are Synthetic Crudes?

- The oil sands of Canada and Venezuela are the source of the synthetic crudes.
- Using refinery units, the heavy bitumen is upgraded to yield products from the oil sands.
- So, the term “synthetic crudes” refers to partially processed, hydrocarbon blends suitable for processing in a crude unit.

Classifying Crude Oil

- Location
- Density (light, heavy) - the scale most commonly used in API Gravity. The higher the number the lighter the crude oil.
  - Generally, the lighter crudes are more valuable since they'll produce more of the higher valued products.
- Sulfur content (sweet, sour)
  - Low sulfur is sweet
  - High sulfur is sour
  - Sweet is usually defined as less than 0.5% sulfur
  - Sweet crudes are more valuable as the sulfur is an undesirable component that must be removed in the refining process.

Are Crude oils all pretty much the same ?

Definitely not.
No more than people are all the same.

Crude Oil Assay Program

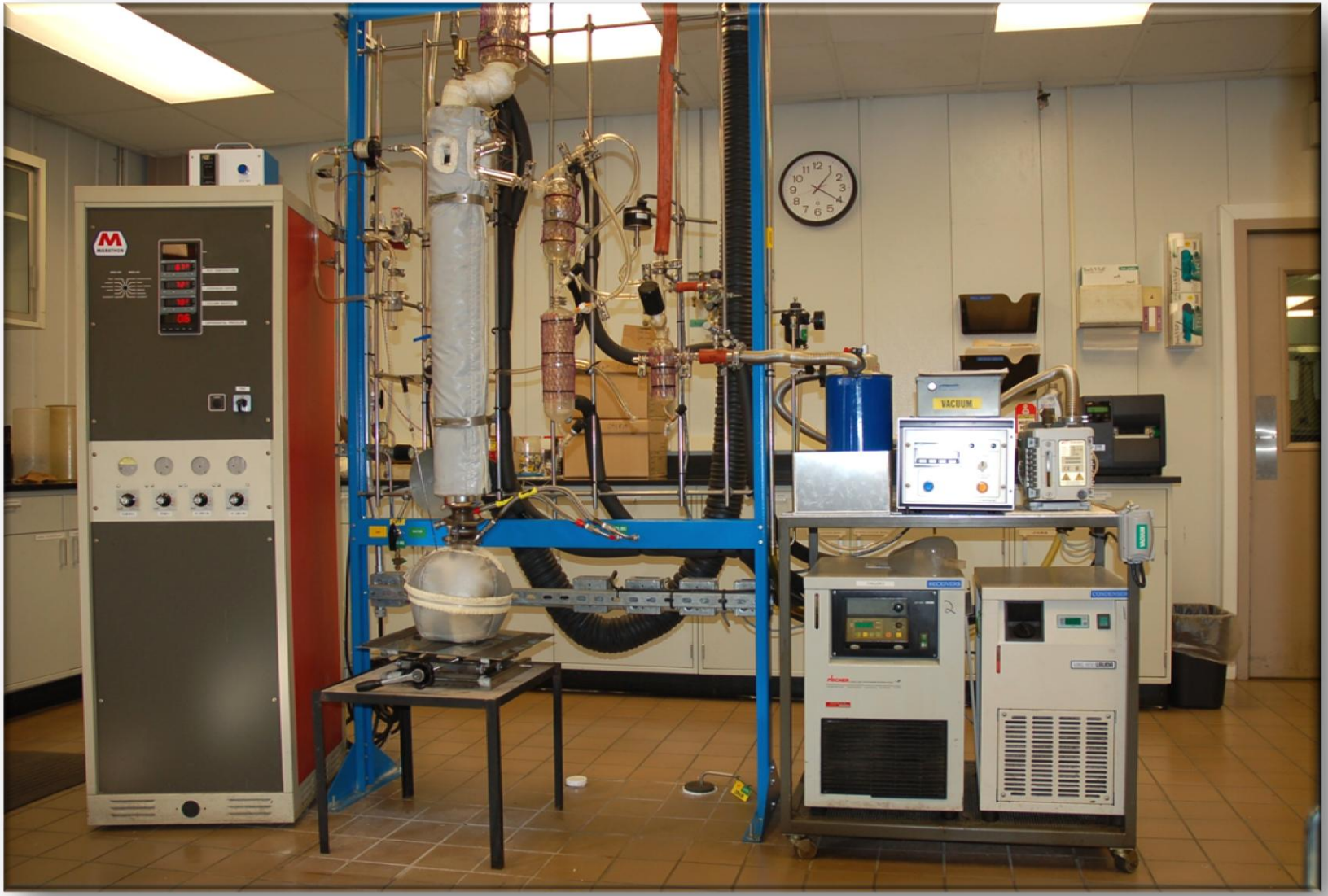
- Crude oils are characterized utilizing a very comprehensive testing slate
- Typical full crude assay cost:
  - $10,000 - $20,000 per crude
- Information is used for:
  - Purchase decisions
  - Refining planning and optimization
  - Capital project decisions

Crude Oil Assay Program

Analytical Testing

- A representative sample of the crude is distilled in the laboratory under similar conditions as the refinery.
- Ten or more boiling range fractions are obtained.
- Very extensive testing is conducted on the whole crude and the various fractions.
- Tests performed are selected based on the products.

Crude Assay Laboratory



Crude Oil Assay Program

Converting Information to Intelligence

- Following the analytical testing, special software programs are used to put the raw analytical data into a form that conclusions, comparisons, and correlations can be made.
- Sophisticated computer models use the crude assay data together with operational data and price information to allow for optimal planning and operation.

Typical Crude Assay

WHOLE CRUDE & SUMMARY OF MAJOR CUTS

	Whole Crude	Light Naphtha	Medium Naphtha	Heavy Naphtha	Kero	Atm Gas Oil	Light VGO	Heavy VGO	Vacuum Resid
TBP Temp At Start, °F	Start	55	175	300	400	500	650	850	1050
TBP Temp At End, °F	End	175	300	400	500	650	850	1050	End
Yield at Start, vol%		0.03	1.13	6.01	11.59	19.96	35.36	58.01	76.31
Yield at End, vol%		1.13	6.01	11.59	19.96	35.36	58.01	76.31	100.00
Yield of Cut (wt% of Crude)		0.79	4.02	4.91	7.74	14.77	22.90	18.93	25.93
Yield of Cut (vol% of Crude)		1.10	4.88	5.58	8.37	15.40	22.65	18.31	23.69
Gravity, °API	20.5	79.2	53.3	41.0	33.0	26.9	18.8	15.5	7.3
Specific Gravity	0.93	0.67	0.77	0.82	0.86	0.89	0.94	0.96	1.02
Sulfur, wt%	0.74	0.00	0.01	0.05	0.16	0.37	0.65	0.90	1.36
Mercaptan Sulfur, ppm		6	13	11	9				
Nitrogen, ppm	4380	0	0	0	4	138	1563	4270	12314
Hydrogen, wt%		16.0	14.3	13.8	13.2	12.6	11.9	11.5	
Viscosity @ 40 °C (104 °F), cSt	64.06	0.60	0.87	1.35	2.21	4.96	39.96	3.51E+03	2.E+08
Viscosity @ 50 °C (122 °F), cSt	40.43	0.54	0.76	1.17	1.85	3.95	26.64	1.06E+03	3.E+07
Viscosity @ 100 °C (212 °F), cSt	8.17	0.38	0.49	0.67	0.95	1.66	6.41	2.81E+01	2.E+04
Viscosity @ 135 °C (275 °F), cSt	4.01	0.33	0.87	1.35	2.21	4.96	39.96	3.51E+03	2.E+08
Freeze Point, °C	63	-118	-106	-90	-72	-44	-10	18	84
Freeze Point, °F	145	-180	-158	-130	-98	-46	14	64	184
Pour Point, °C	-24	-124	-112	-93	-74	-48	-16	11	87
Pour Point, °F	-11	-191	-169	-135	-100	-54	4	52	188
Smoke Point, mm (ASTM)	4	32	26	19	15	11	6	3	2
Aniline Point, °C	69	70	46	46	52	56	64	79	91
Aniline Point, °F	156	157	114	114	125	133	147	174	196
Total Acid Number, mg KOH/g	0.80	0.0	0.1	0.2	0.4	0.7	0.5	0.5	0.5
Cetane Index, ASTM D4737				29	34	40			
Diesel Index	32	125	61	47	41	36	28	27	14
Characterization Factor (K Factor)	11.6	12.5	11.6	11.4	11.3	11.3	11.3	11.6	11.8
Paraffins, vol%		77.9	23.5	23.3	17.1				
Naphthenes, vol%		22.1	69.4	65.7	63.5				
Aromatics, vol%		0.0	7.1	11.0	18.9				
Heptane Asphaltenes, wt%	1.8								6.8
Micro Carbon Residue, wt%	5.2								19.3
Ramsbottom Carbon, wt%	5.1								18.8
Vanadium, ppm	17								66
Nickel, ppm	11								41
Iron, ppm	5								20

Other Non-Crude Refinery Feedstocks

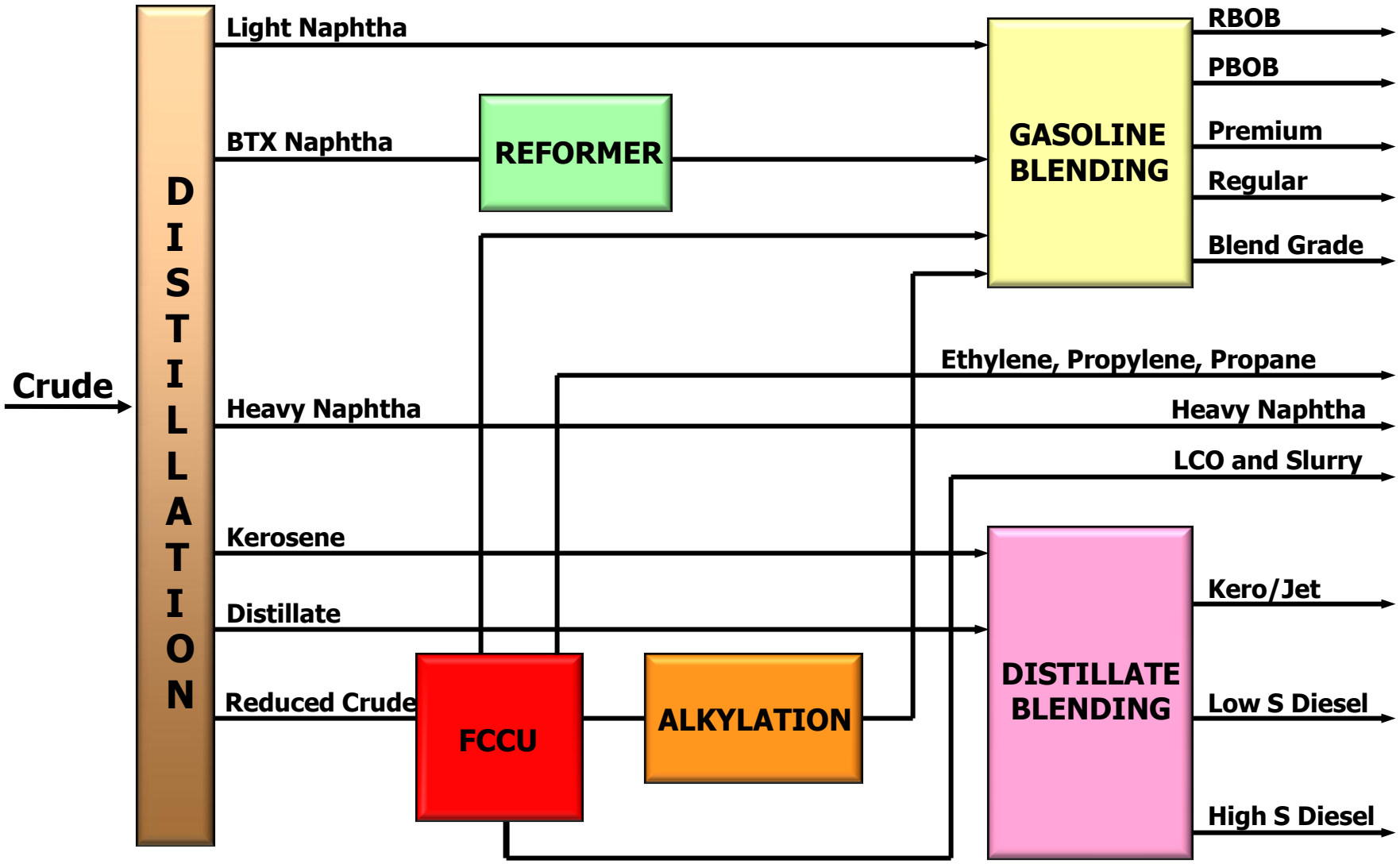
- Gas oil, feed to the cat cracker
- Gasoline blendstocks - intermediate materials to be blended into the finished gasoline
- Butane(s)
- Raw materials for specialty units


REFINERIES are
like snowflakes…
no two are the same!!

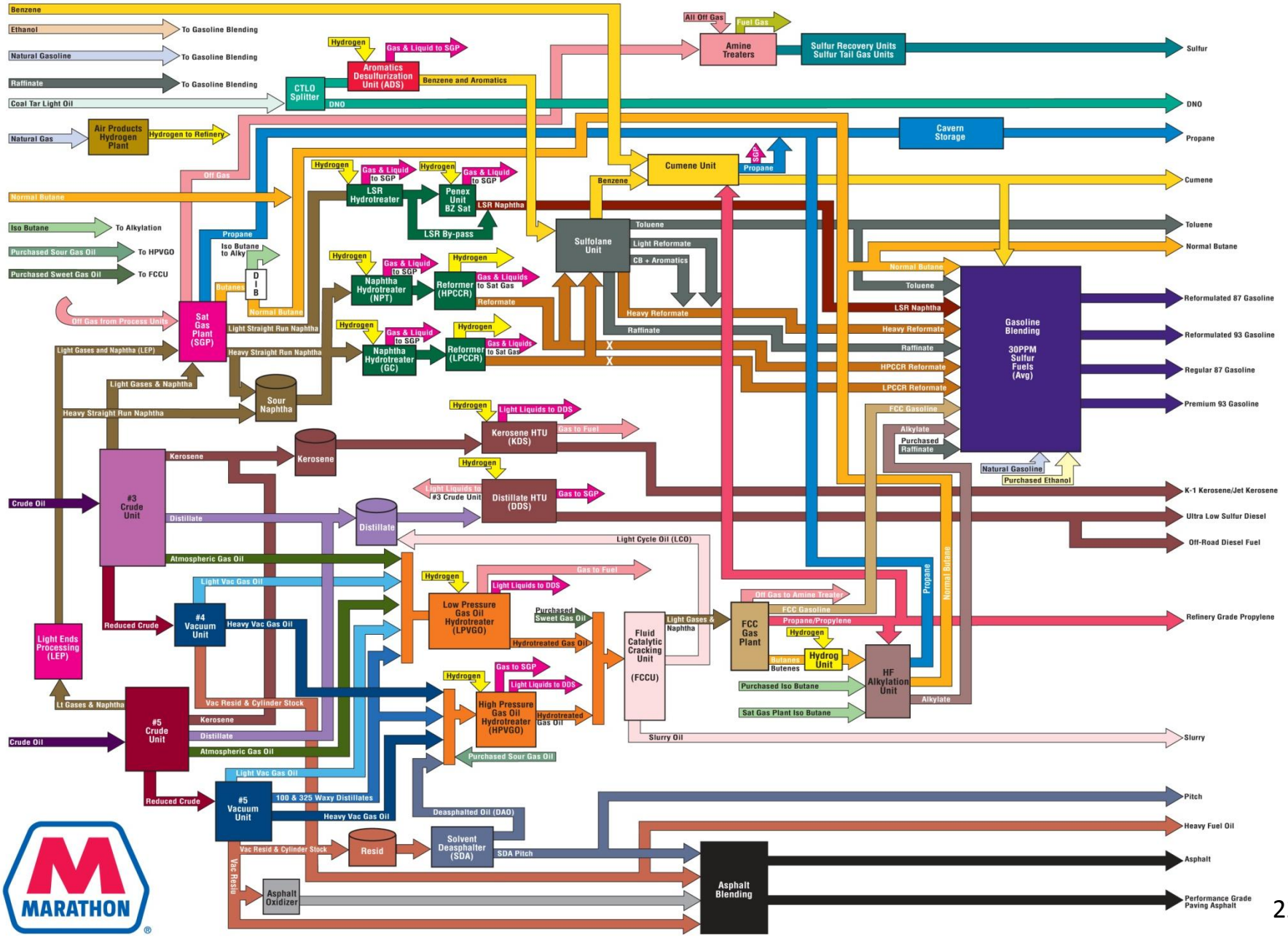
Refinery Configuration Factors

- Process Units (Type & Size)
- Location
- Transportation Options
- Tankage

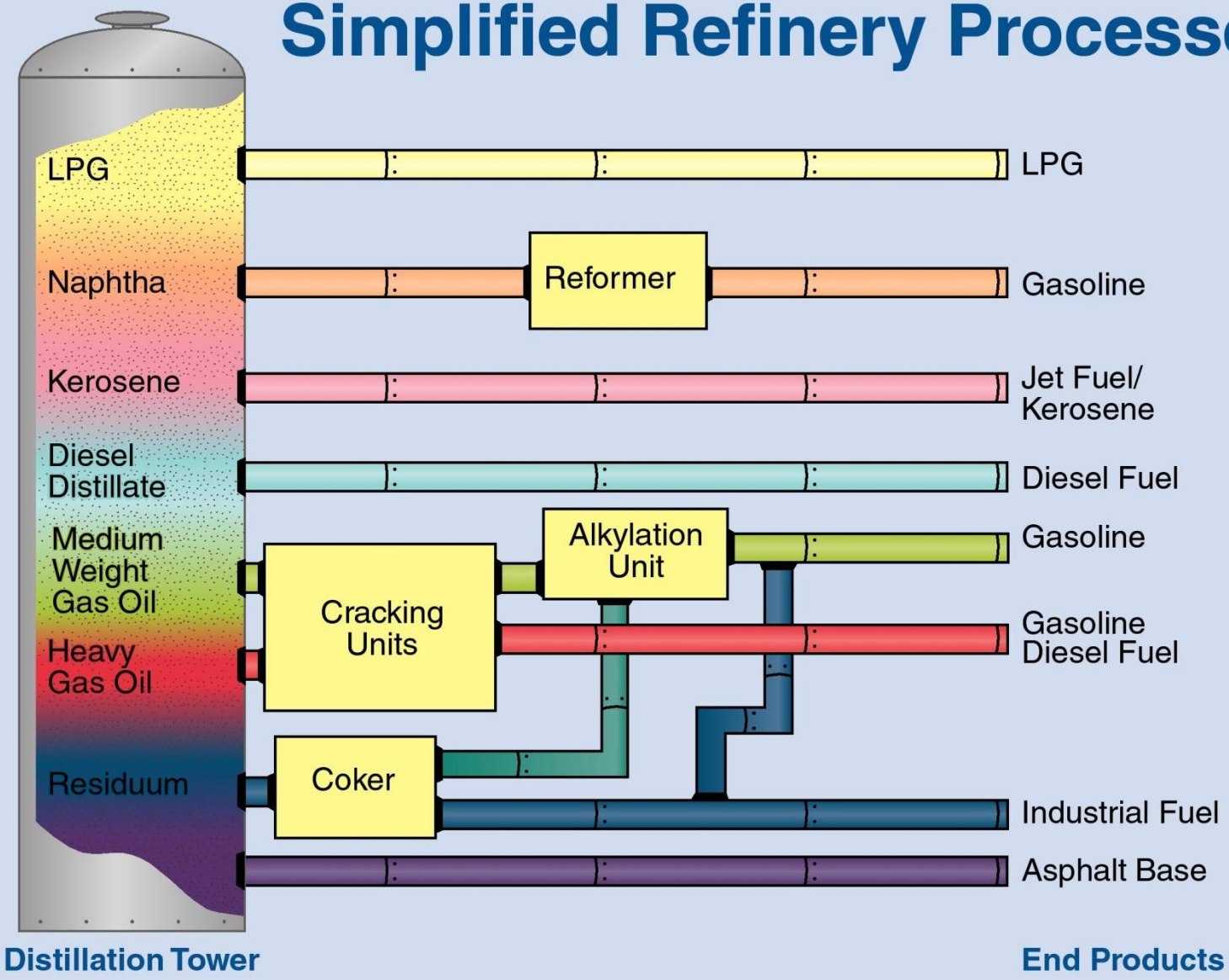
A Very Simple Refinery



Catlettsburg Refinery • Simplified Flow Chart • 100% Low Sulfur Fuels Refinery



Simplified Refinery Processes



Refining Process

Refining Crude Into Useful Products

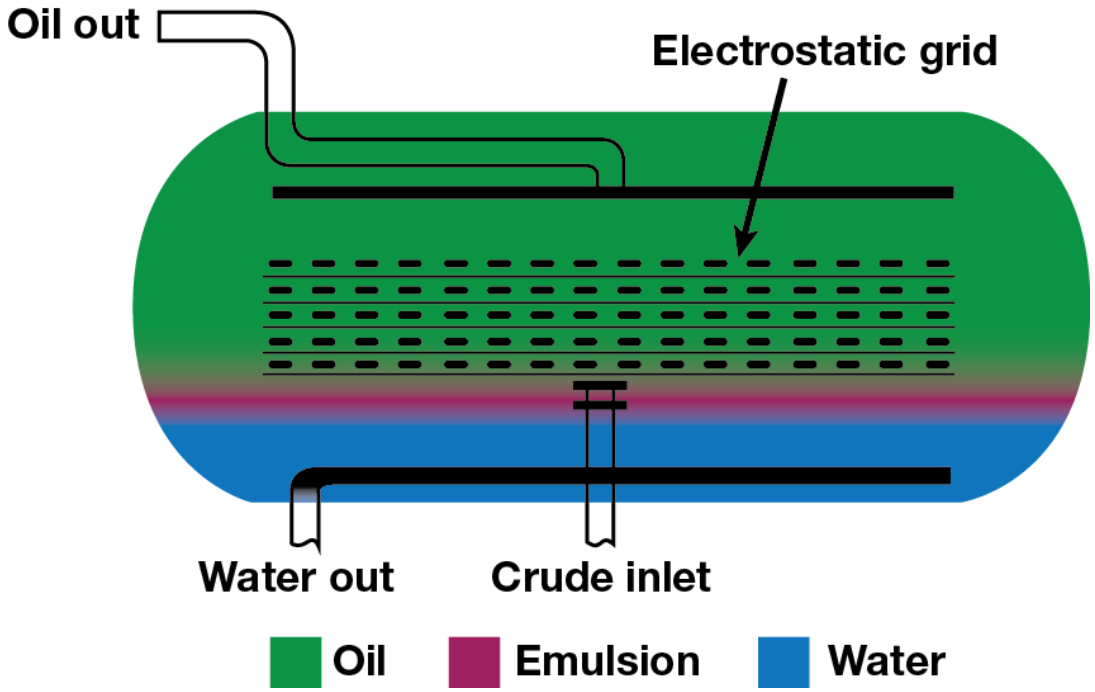
- Physical Processes
  - Separate hydrocarbon compounds based on physical characteristics without causing chemical reactions
    - Boiling point
    - Solubility in selected solvent
  - No change to hydrocarbon structures
    - Distillation

Refining Crude Into Useful Products

- Chemical Processes
  - Alter chemical structure of hydrocarbon molecules
    - Example: rearrange molecules into ones with more desirable properties
  - Change the size of hydrocarbon molecules
    - Example: break large molecules into several smaller ones
    - Example: combine several small molecules into larger ones
  - Remove impurities such as sulfur and nitrogen

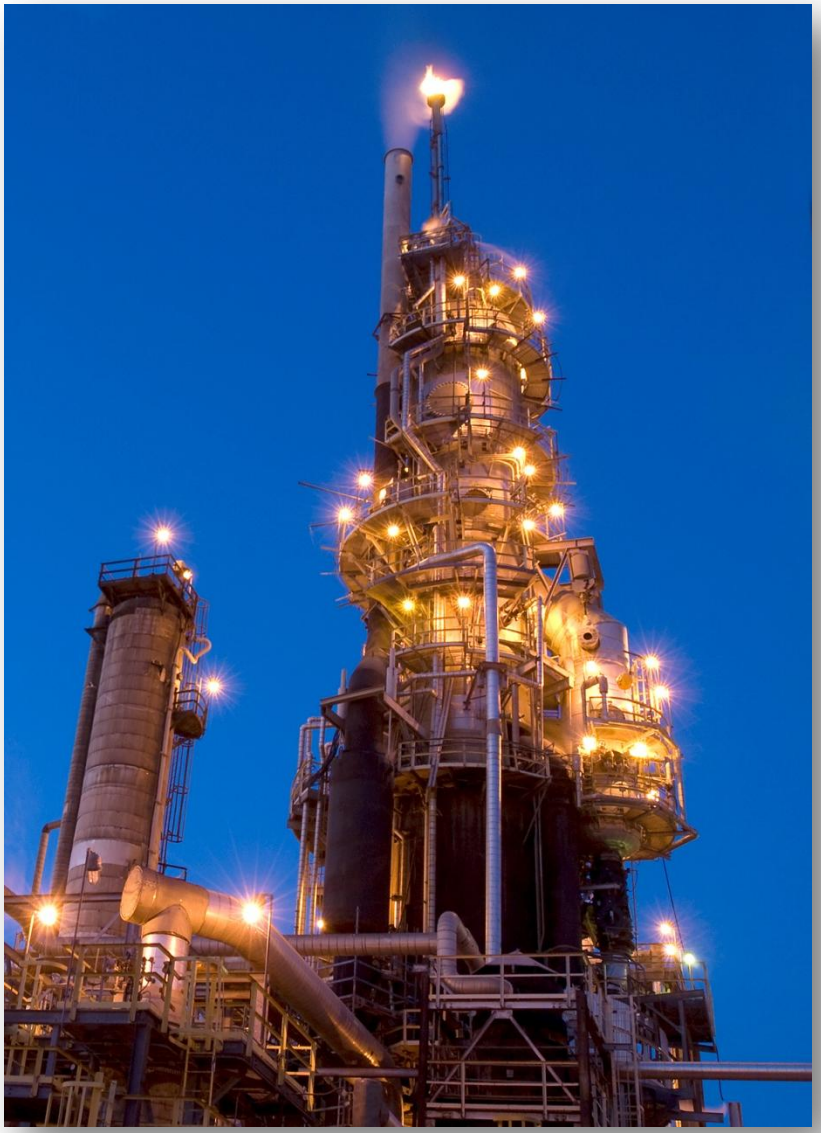
Desalting

- Prior to introducing the crude to the main units, it must be "cleaned."
- By using chemicals, heat, and electrical fields, the sediment, salts, and water are removed.



Distillation

- Primary physical separation process within the refinery
- Separates hydrocarbon mixtures according to boiling point
- Used in various places in the refinery



Refining Processes Involving Chemical Reactions

Reforming

Cracking

Hydrotreating

Alkylation

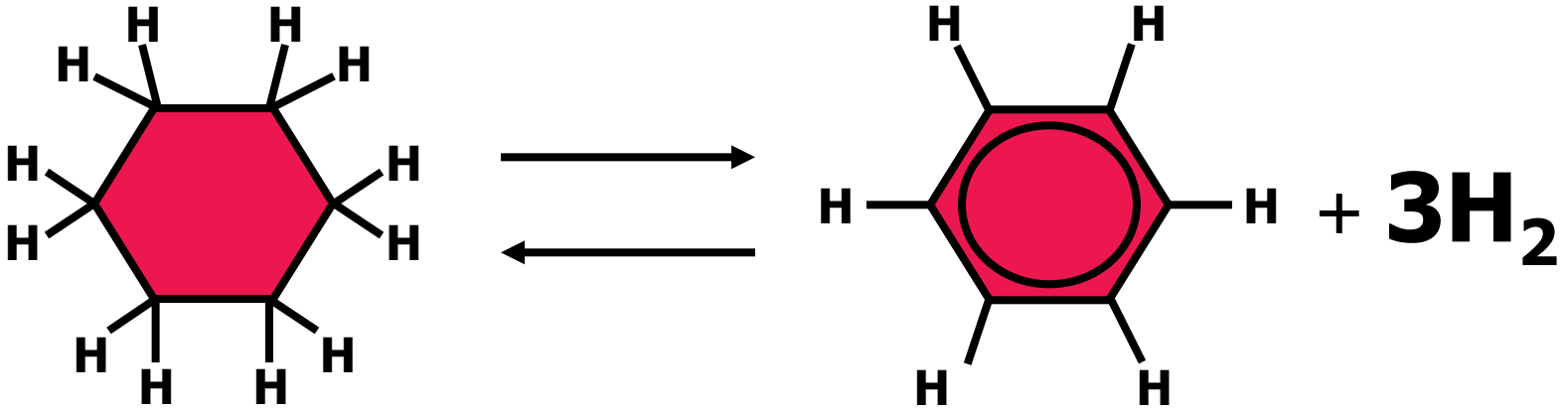
Coking

Catalytic Reforming

- Function is to chemically alter “naturally-occurring” gasoline-like material (naphtha) to boost its octane
- Converts low octane paraffins and naphthenes into high octane aromatics

Catalytic Reforming – Primary Process Chemistry

- Dehydrogenation of naphthenes to aromatics



C_6H_{12} $\quad$ Benzene- C_6H_6

RON 80 $\quad$ **115**

(an example)

Catalytic Cracking

- Function is to “crack” the gas oil (650°F- 1000 °F) fraction of the crude oil to produce more gasoline and distillate fuels
- Usually uses a fluidized catalyst - thus Fluidized Catalytic Cracking Unit (FCCU)
- FCC was developed since the amount of naphtha in crude oil is insufficient to meet the demand for gasoline per barrel of crude

Hydrotreating

- Removes sulfur (and nitrogen) compounds from intermediate feedstocks
- Hydrotreating is necessary to meet low sulfur product quality specifications
- Uses hydrogen produced by reformers

Alkylation

- "Links" small molecules together to yield high octane, low vapor pressure gasoline blendstock

Alkylate Product

An Ideal "Green" Gasoline Blendstock

- Very high octane
- NO sulfur
- NO aromatics
- NO olefins
- NO benzene
- Can be low vapor pressure

Coking

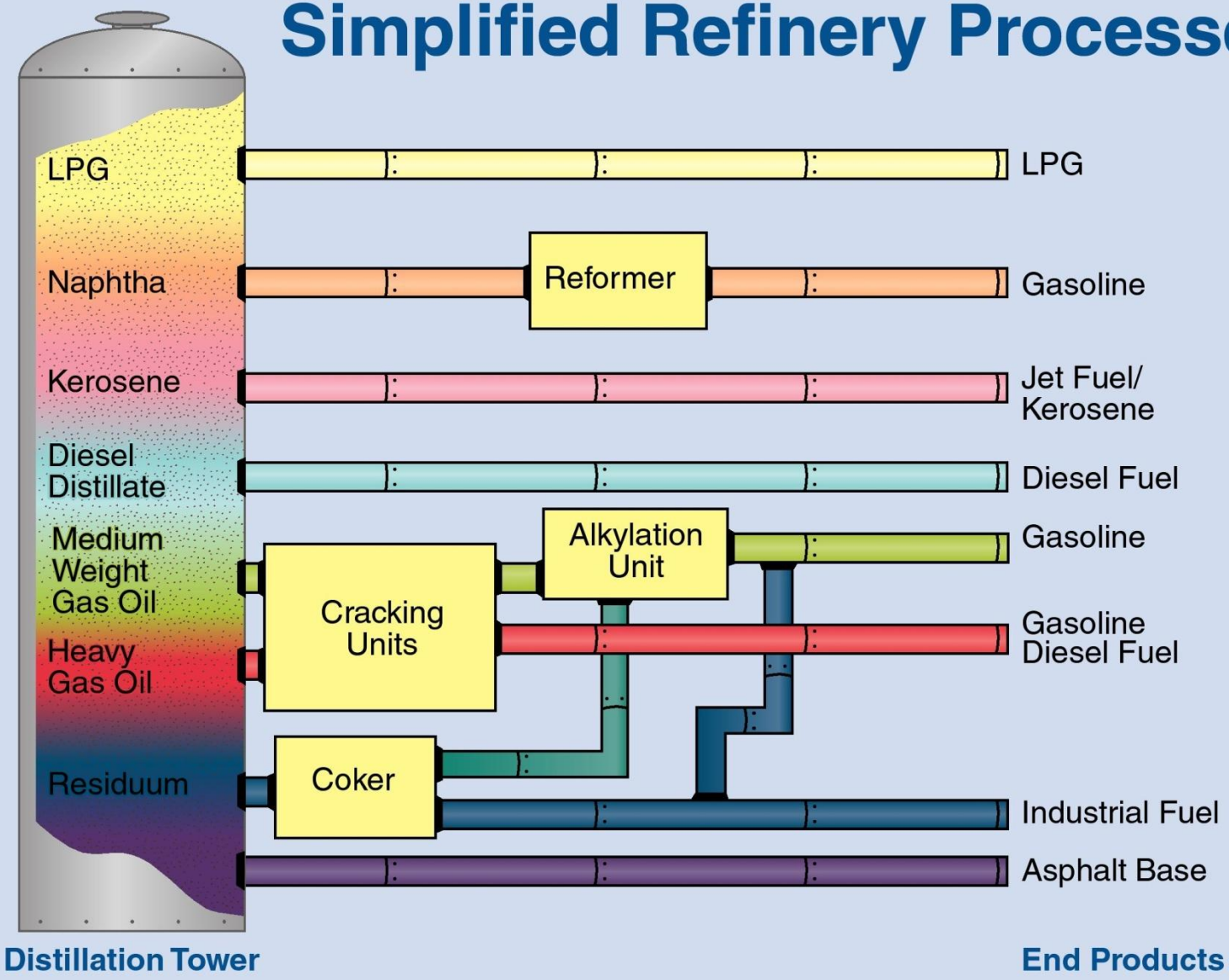
- A method of bottoms upgrading
- Feedstock:
  - Vacuum resid – heaviest
  - Highest boiling crude fraction
  - High sulfur
  - High metals
- Products:
  - 6-10% gas
  - 15-20% naphtha
  - 35-60% gas oil
  - 20-40% coke

What Products do we make?

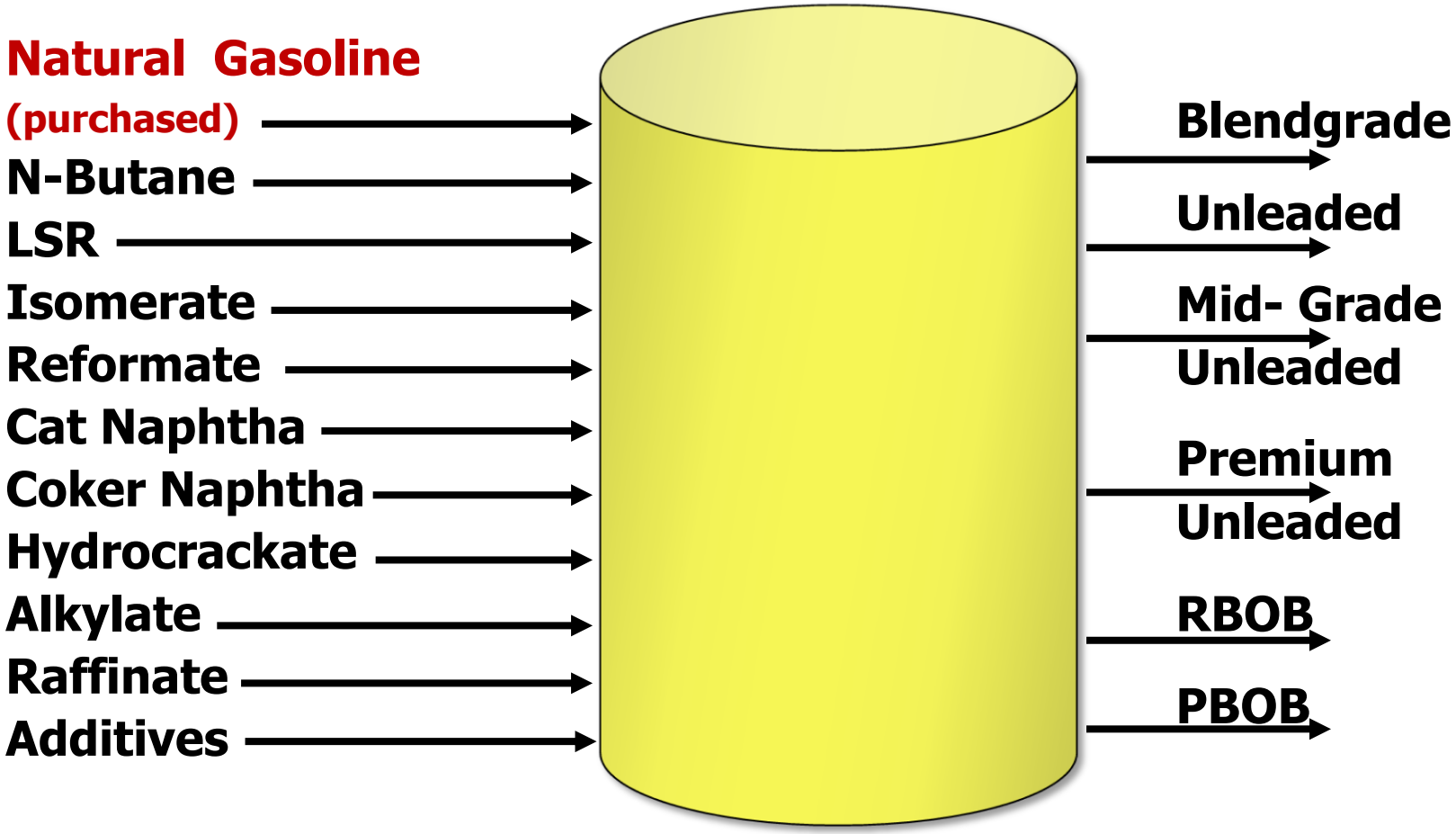
Petroleum Refinery Products

- Propane and Propylene
- Butane(s)
- Specialty Solvents
- Specialty Products
  - Benzene
  - Toluene
  - Cumene…
- Gasoline - various grades
- Kerosene
- Jet Fuel
- Diesel Fuel - various grades
- Heavy Fuel Oils
  - No. 4, No. 6, etc.
- Roofing Flux
- Road Asphalt - various grades
- Petroleum Coke

Simplified Refinery Processes



Gasoline Blending (at the Refinery)



Typical Gasoline Specifications
87 Regular Conventional

Specification	Test Method	Unit	Minimum	Maximum	Text
Workmanship	N/A				Clear, Bright, Particulate Free
Gravity - API	ASTM D4052; Calculation; D1298; D287	degrees API			Report Only
Copper Strip Corrosion	ASTM D130			1	Test conducted at 122deg F for 3hrs
Silver Strip Corrosion	D4814 Annex			1	Test conducted at 122deg F for 3hrs
NACE	NACE TM0172				B+ min
Oxidation Stability	ASTM D525	minutes	240		
Washed Gum	ASTM D381	mg/100 ml		4	
Sulfur w/ethanol	D7039; D5453; ASTM D2622	wt.ppm			Report Only
Sulfur	D2622; D7039; D5453	wt.ppm		80	
Lead	D3237; ASTM D3341	g/Gallon		0.05	
Phosphorous	ASTM D3231	g/Gallon		0.005	
Doctor	ASTM D4952				Negative
Mercaptan Sulfur	ASTM D3227	wt.ppm		20	
Oxygenates	D5599	wt%		0.100	
End Point w/ethanol	ASTM D86	°F		430	
End Point	ASTM D86	°F		430	
Residue w/ethanol	ASTM D86	percent		2	
Residue	ASTM D86	percent		2.0	
RON	ASTM D2885; NIR; ASTM D2699				Report
MON	ASTM D2885; NIR; ASTM D2700		82.0		
(R+M)/2	ASTM D2885; NIR; ASTM D2700		87.0		

HTSUS Overview

Crude Oil	
<25° API	2709.00.10
≥25° API	2709.00.20

Other Feedstocks	
Butane	2711
Gas Oil and Other Blend Stocks	2710

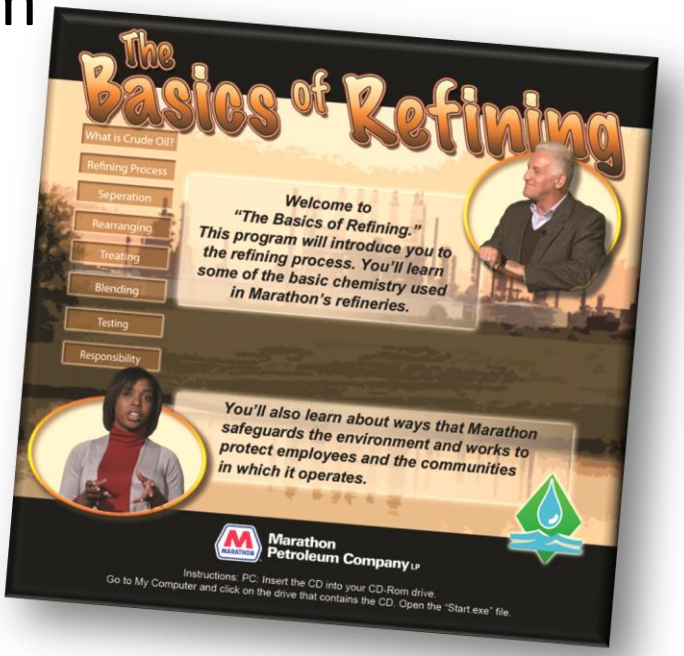
Products	
Propane	2711
Gasoline	2710.12
Kerosene	2710.19
Diesel	2710.19
Asphalt	2713.20
Petroleum Coke	2713.90

Specialty Products	
Benzene & Toluene	2707 2902
Cumene	2902

Safely, and efficiently transform crude oil and other raw materials into on-spec finished products.

Refining Resources

- Marathon Petroleum “The Basics of Refining” multi-media program



- “Petroleum Refining in Nontechnical Language,” by William L. Leffler

Questions?