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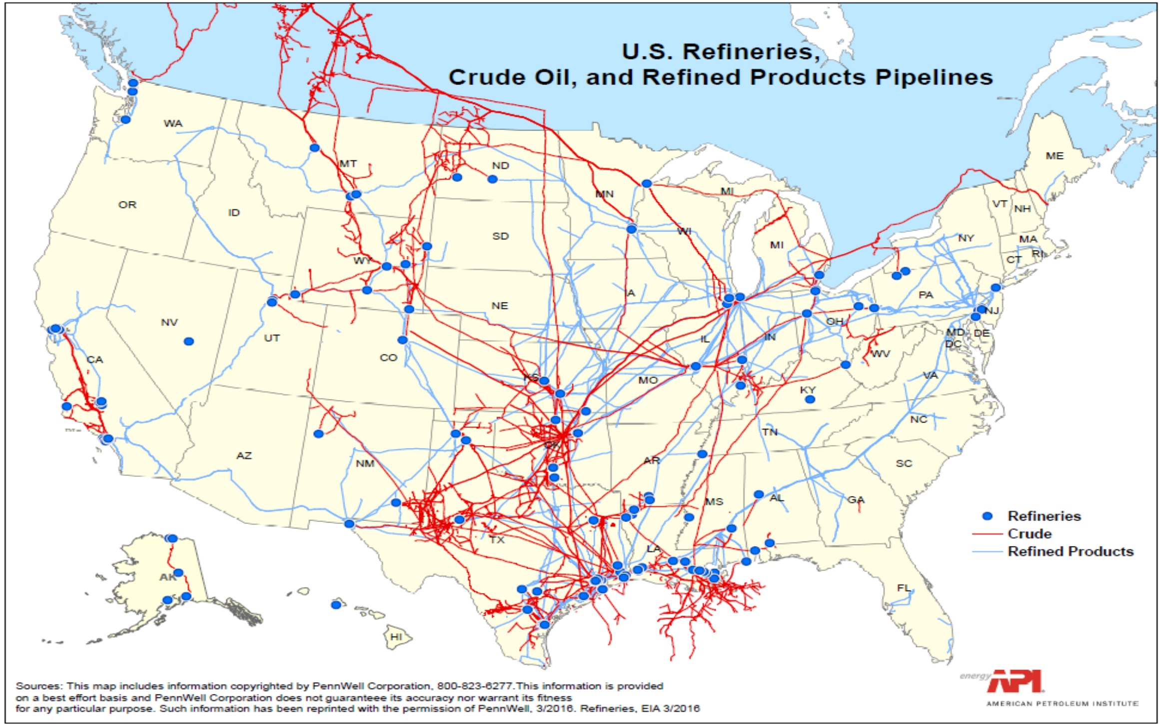
REFINING 101

By Ben Gonzalez

OUTLINE

- Crude
- Hydrocarbon Chemistry
- Refinery Types
- Refining Units
- Gasoline Blending
- Refining Economics

US REFINERIES



https://www.eia.gov/petroleum/refinerycapacity/

- Total of 133 refineries in US based on crude distillation units
- Total crude distillation capacity is 18.3 mmbpd
- PADD 3 or the USGC region makes up 53% of crude distillation capacity; total of 54 refineries.
- Crude distillation capacity in the East Coast or PADD 1 is ~1.2 mmbpd
- PADD 2 or the Midwest, has less refineries than the West Coast but has the second largest capacity with ~4 mmbpd
- PADD 4 or the Rockies has more refineries than the East Coast but has the least capacity with only 682 mbpd
- PADD 5 or the West Coast has a capacity of 2.8 mmbpd.

LARGEST US REFINERS

Rank	Corporation	Barrels/Day	No. of US Refineries
1	VALERO ENERGY CORP	2,180,300	13
2	MARATHON PETROLEUM CORP	1,817,000	7
3	EXXON MOBIL CORP	1,725,400	5
4	PHILLIPS 66 COMPANY	1,615,200	9
5	MOTIVA ENTERPRISES LLC	1,056,386	3
6	CHEVRON CORP	908,771	4
7	TESORO CORP	863,600	8
8	PBF ENERGY CO LLC	843,100	5
9	PDV AMERICA INC	758,440	3
10	BP PLC	647,000	3

Source: US Energy Information Administration, Table 5, 2015.

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THE CRUDE

CRUDE

- Crude oil and natural gas are a mixture of hydrocarbons, and small amounts of impurities such as oxygen, nitrogen, sulfur, salt, water, and certain metals.
- Crude is piped from the reservoir as a mixture of different hydrocarbons ranging from light gases to heavy pitch.
- Crude can be light or heavy, with little sulfur (sweet) or with higher sulfur (sour).

Leffler, William (2000). Petroleum Refining in Nontechnical Language

GRAVITIES

- API Gravity – an index by the American Petroleum Institute that measures in degrees the weight of the compound
- API $= \frac{141.5}{specific\ gravity} - 131.5$
- Specific Gravity $= \frac{weight\ of\ compound}{weight\ of\ water}$
- Water has a specific gravity of 1 and an API gravity of 10°
- The higher the API gravity the lighter the compound, and vice versa.

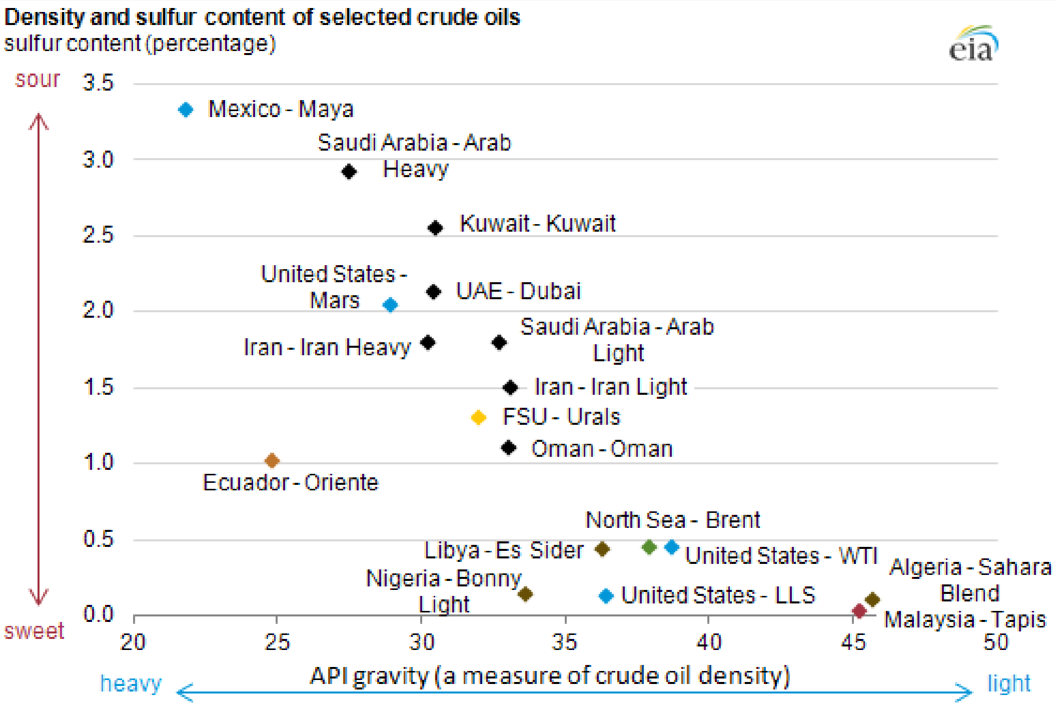
Source: Weatherford Laboratories http://labs.weatherford.com/services/laboratory-services/geochemistry/oil-geochemistry/api-gravity

Leffler, William (2000). Petroleum Refining in Nontechnical Language

SYNTHETIC CRUDES

- Processed heavy bitumen from source, ground or oil sands, to form feedstock blends for refineries.
- Oil sands are a loose sand deposit containing bitumen.
- Bitumen is a heavy complex tar-like hydrocarbon
- Most bitumen is diluted with condensate, other is upgraded to synthetic crude.
- Mainly sourced from Venezuela and Canada
- Conversion units such as cokers are used to upgrade the bitumen, thus yielding coke as by-product

Source: Oil Sands Magazine
http://www.oilsandsmagazine.com/technical/oilsands-101



Typical API Gravities

Light	>31.1°
Medium	between 22.3° and 31.1°
Heavy	<22.3°
Extra Heavy	<10°
Gasoline	60°
Asphalt	11°

Source: EIA
https://www.eia.gov/todayinenergy/detail.php?id=7110

US REFINERY THROUGHPUT

Share of Crude Quality Inputs (excluding condensates)

	2007	2013	2014	2015	2016
Heavy (<=24°API)	25%	25%	24%	26%	27%
Medium (>24 - 30.9°API)	24%	19%	20%	15%	13%
Light (>30.9 - 41.9°API)	45%	41%	39%	38%	36%
Super Light (>41.9 - 50°API)	7%	14%	17%	21%	24%

Total Refinery Actual and Planned Inputs of Crude Oil by Gravity

	2007	2013	2014	2015	2016	Percent Increase 2007-2016	Volume Change 2014-2015
Heavy (<=24°API)	2,187	2,469	2,442	2,718	2,798	28%	356
Medium (>24 - 30.9°API)	2,042	1,867	1,963	1,542	1,291	-37%	-672
Light (>30.9 - 41.9°API)	3,855	4,033	3,890	3,980	3,659	-5%	-231
Super Light (>41.9 - 50°API)	565	1,411	1,723	2,149	2,456	335%	733
Condensate (>50°API)	D	D	D	D	D	D	D
Total Excl. Condensate	8,649	9,780	10,018	10,389	10,204	18%	186

AFPM (2015) Refining U.S. Petroleum: A Survey of U.S. Refinery Use of Growing U.S. Crude Oil Production https://www.afpm.org/uploadedFiles/Refining-US-Capacity.pdf

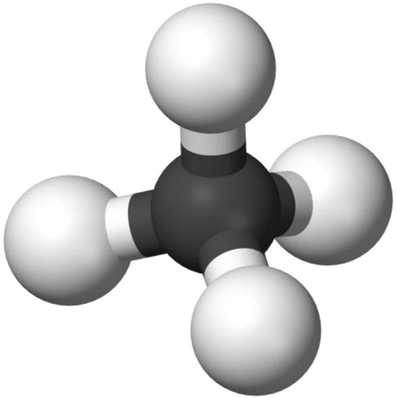
TYPICAL CRUDE ASSAY

- No crudes are the same
- Crude oil assay is a chemical evaluation of crude oil feedstocks
- Used for purchasing, planning, optimization, and capital investment decisions.

1. Leffler, William (2000). *Petroleum Refining in Nontechnical Language*

2. http://corporate.exxonmobil.com/en/company/worldwide-operations/crude-oils/assays

BRENT16X	Whole crude	Butane and Lighter IBP - 60F	Lt. Naphtha C5 - 165F	Hvy Naphtha 165 - 330F	Kerosene 330 - 480F	Diesel 480 - 650F	Vacuum Gas Oil 650 - 1000F	Vacuum Residue 1000F+
Cut volume, %	100.0	2.9	9.2	21.3	15.6	16.7	24.5	9.7
API Gravity,	40.1	124.6	89.7	56.6	42.8	32.3	22.7	16.1
Specific Gravity (60/60F),	0.825	0.552	0.640	0.752	0.812	0.864	0.918	0.959
Carbon, wt %	86.0	82.4	83.7	86.0	85.9	86.4	86.5	86.4
Hydrogen, wt %	13.6	17.6	16.3	14.0	14.1	13.4	12.9	12.3
Pour point, F	13.1			(132.8)	(71.4)	10.1	82.8	89.7
Neutralization number (TAN), MG/GM	0.064	0.073	0.074	0.074	0.053	0.022	0.075	0.088
Sulfur, wt%	0.347	0.000	0.000	0.001	0.014	0.207	0.578	1.330
Viscosity at 20C/68F, cSt	7.0	0.4	0.5	0.8	1.7	6.9	244.7	3,337,634.5
Viscosity at 40C/104F, cSt	3.5	0.4	0.4	0.6	1.3	4.0	66.1	137,033.9
Viscosity at 50C/122F, cSt	2.6	0.3	0.4	0.6	1.1	3.2	39.5	38,389.0
Mercaptan sulfur, ppm	1.0	0.1	0.4	2.3	3.4	1.2	0.2	0.0
Nitrogen, ppm	898.4	-	-	0.0	0.9	45.1	933.8	5,610.9
CCR, wt%	2.1						0.2	17.8
N-Heptane Insolubles (C7 Asphaltenes), wt%	0.2						-	2.0
Nickel, ppm	1.2							10.9
Vanadium, ppm	6.3							55.9
Calcium, ppm	0.5							
Reid Vapor Pressure (RVP) Whole Crude, psi	10.3							
Hydrogen Sulfide (dissolved), ppm	-							
Salt content, ptb	-							
Paraffins, vol %	39.6	100.0	87.5	46.1	46.7	36.3	24.3	2.8
Naphthenes, vol %	33.2	-	12.5	36.8	37.2	43.0	39.7	20.9
Aromatics (FIA), vol %	27.2	-	-	17.1	16.2	20.7	36.1	76.4
Distillation type, TBP								
IBP, F	(9.1)		60.7	166.0	330.7	480.8	651.3	1,001.1
5 vol%, F	83.7		66.9	174.3	337.2	488.2	663.5	1,011.1
10 vol%, F	144.7		71.9	183.2	344.5	496.4	677.2	1,022.6



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HYDROCARBON CHEMISTRY

CLASSIFICATIONS

- Organic Chemistry – study of the structure of properties, composition, reactions, and preparation of carbon-containing compounds, including hydrocarbons.
- Hydrocarbons, compounds that contain only carbon and hydrogen, are the principal constituents of petroleum and natural gas, and can be classified into three categories
  - Aliphatics – alkanes (paraffins), alkenes (olefins), and alkynes.
  - Cycloaliphatics (cycloalkanes or naphthenes)
  - Aromatics

1. https://www.britannica.com/science/hydrocarbon

ALKANES

Paraffins - Straight Chain Compounds, saturated hydrocarbons, having formula C_nH_{2n+2}.

Formula	Name	Formula	Name
CH_4	Methane	C_6H_{14}	Hexane
C_2H_6	Ethane	C_7H_{16}	Heptane
C_3H_8	Propane	C_8H_{18}	Octane
C_4H_{10}	Butane	C_9H_{20}	Nonane
C_5H_{12}	Pentane	$C_{10}H_{22}$	Decane

1. Leffler, William (2000). Petroleum Refining in Nontechnical Language

2. https://www.britannica.com/science/hydrocarbon

ALKENES

- Olefins – Unsaturated hydrocarbons, containing a carbon-carbon double bond
- Main Olefins: Ethylene, Propylene, Butylene
- Key characteristic is absence of two hydrocarbons, formula C_nH_{2n}
- Chemically unstable, can be reacted with some other compound with ease

1. Leffler, William (2000). Petroleum Refining in Nontechnical Language

2. https://www.britannica.com/science/hydrocarbon

CYCLOALKANES

- Also known as naphthenes
- Class of hydrocarbons bent into ring or cyclic shape with formula C_nH_{2n}
- Examples: cyclopropane, cyclobutane, cyclopentane, cyclohexane, etc.

1. *Leffler, William (2000). Petroleum Refining in Nontechnical Language*

2. *https://www.britannica.com/science/hydrocarbon*

AROMATICS

- Based on the benzene ring
  - A cyclohexane ring with a hydrogen atom removed from each carbon, and satisfying valence rules by putting double bonds between carbons.
- Referred to BTXs: Benzene, Toluene, and Xylenes
- Double bonds make the benzene ring unstable, used as building block in chemical industry
- Name aromatics came by characteristic smell of BTXs

1. Leffler, William (2000). Petroleum Refining in Nontechnical Language

2. https://www.britannica.com/science/hydrocarbon

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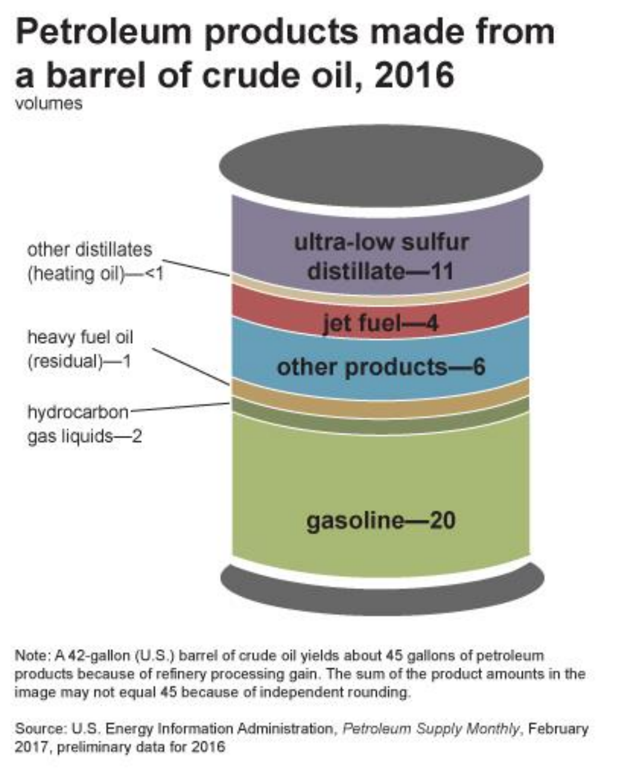
REFINERY TYPES

REFINERY CRUDE DIET

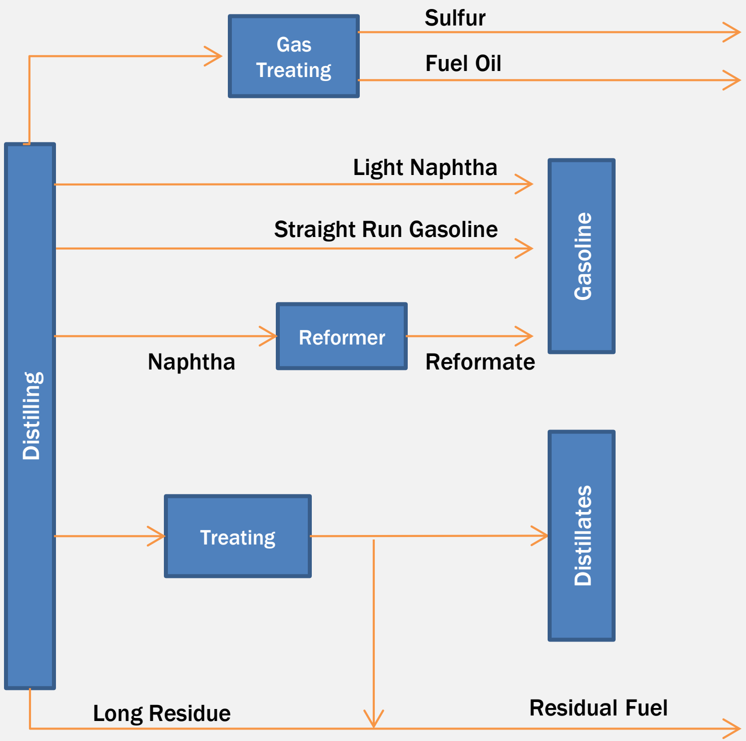
- No crudes are the same
- No refineries are the same
- Refinery Configuration Factors
  - Process units
  - Location
  - Infrastructure
  - Logistics Options



Source: EIA
https://www.eia.gov/energyexplained/?page=oil_home

SIMPLE REFINERY

- Crude distillation,
- Cat reforming, and
- Distillates Hydrotreaters



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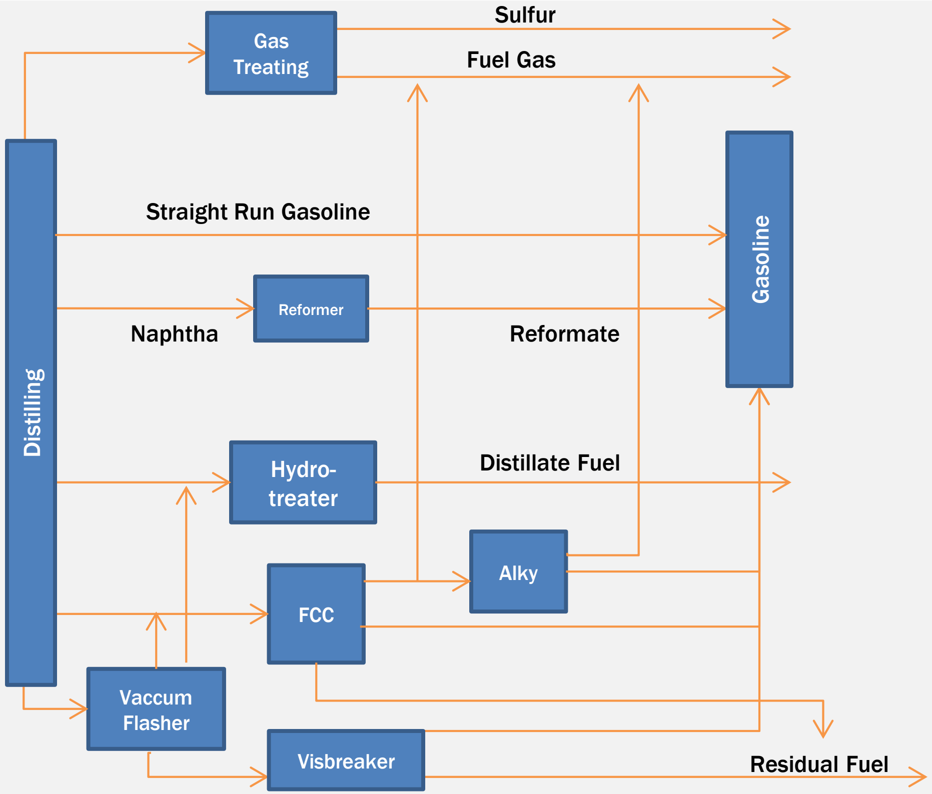
COMPLEX REFINERY

- Simple refinery plus
- Cat cracker (FCC)
- Alky plant
- Gas processing



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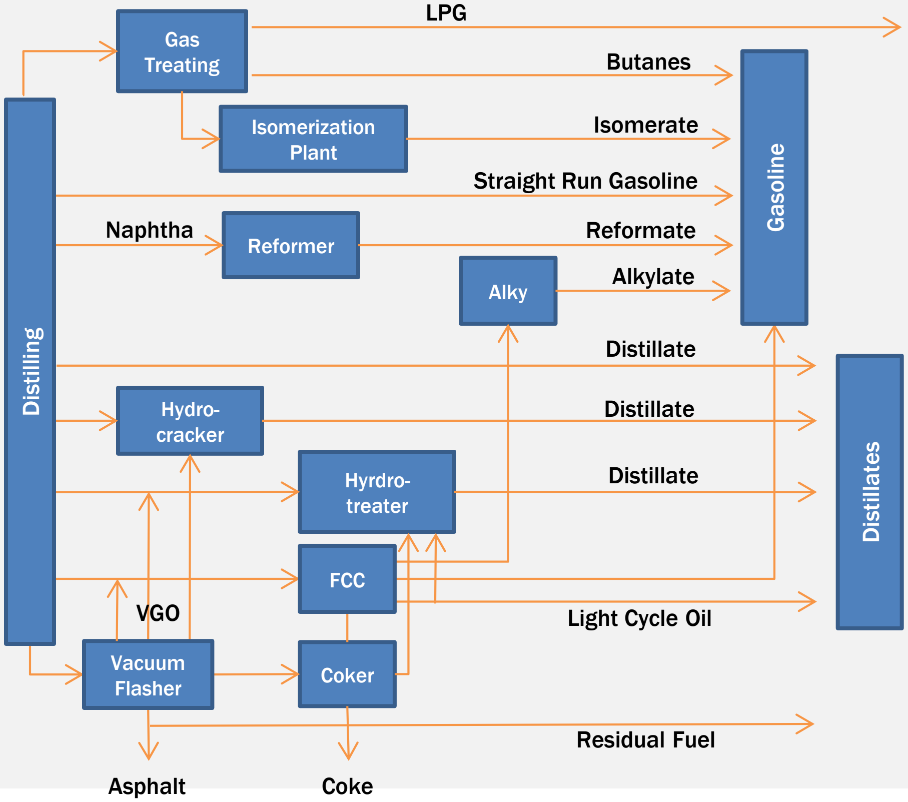
VERY COMPLEX REFINERY

- Complex Refinery plus
- Coker



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THE NELSON COMPLEXITY INDEX

- The Nelson Complexity Index is the measure of complexity.

$$\sum_{i=1}^{N} F_i * \frac{C_i}{C_{CDU}}$$

- F_i is complexity factor = assigned to unit
  - For example, if unit costs 3 times more than the CDU, then it would have a complexity factor of 3.
- C_i is unit capacity
- C_{CDU} is capacity of Crude Distillation Unit
- N is the number of all units

A refinery with a cat cracker, alky unit, and hydrotreating unit may have a factor of 7 while one with a cracker, alky unit, hydrocracking unit, reformer and coking unit may have a factor of 14.

Johnston, Daniel (1996) Refining Report Complexity index indicates refinery capability, value
http://www.ogj.com/articles/print/volume-94/issue-12/in-this-issue/general-interest/refining-report-complexity-index-indicates-refinery-capability-value.html

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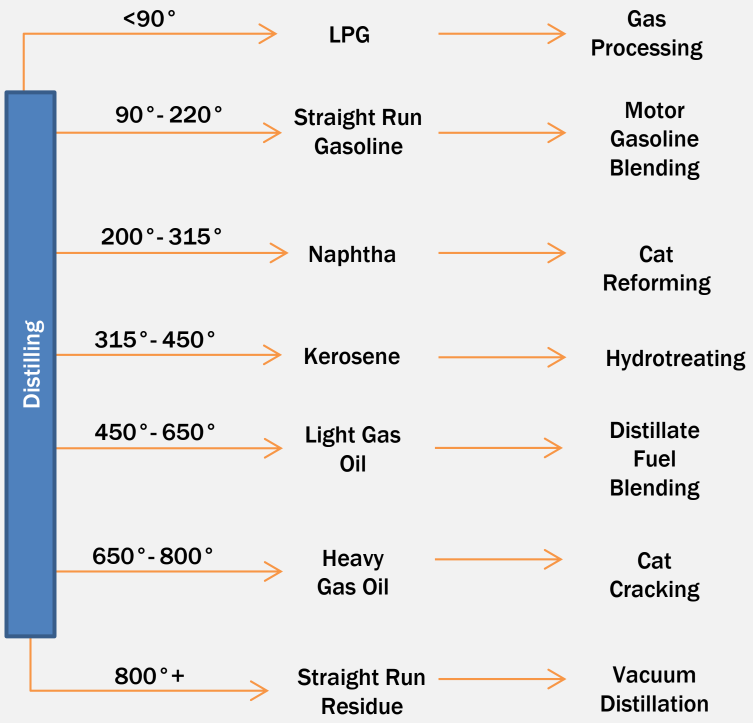
REFINING UNITS

CRUDE DISTILLATION

- Primary physical separation process
- Combination of liquid and vapor introduced to distilling column
- Separates according to boiling point
- Column has set of trays with perforations allowing vapors to rise through column
- Temperature at which product begins to boil is called the initial boiling point (IBP)
- Temperature at which it is 100% vaporized is the end point (EP)



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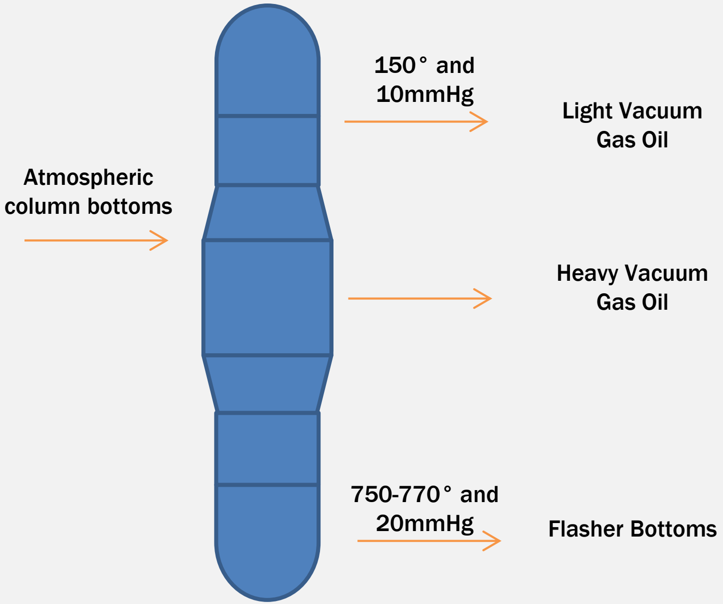
VACUUM DISTILLATION UNIT

- Feed is straight run residue from the distillation unit
- Separated into reduced cuts using distillation at reduced pressure
- Vacuum tops are hydrotreated or used as feed for the FCC unit
- Vacuum bottoms are converted using as feed for thermal cracker, coker, or asphalt unit
- About 80% of refineries in the US have a VDU



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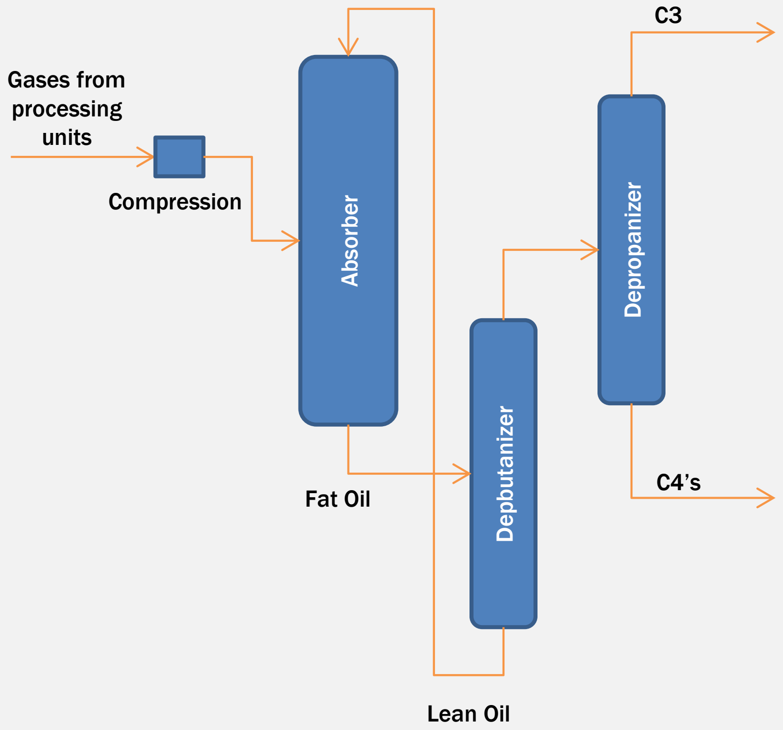
SAT GAS PROCESSING

- Gas streams from the refinery process units have only saturates (i.e. methane, ethane, propane, butanes)
- In order to get streams to liquefy, the mixture must be supercooled or put under pressure, or combination
- Feed is compressed, then introduced to an absorber
- Lean Oil (naphtha range liquid) absorbs most of the propane and butane, together known as fat oil
- Fat Oil is then charged to debutanizer, then to depropanizer



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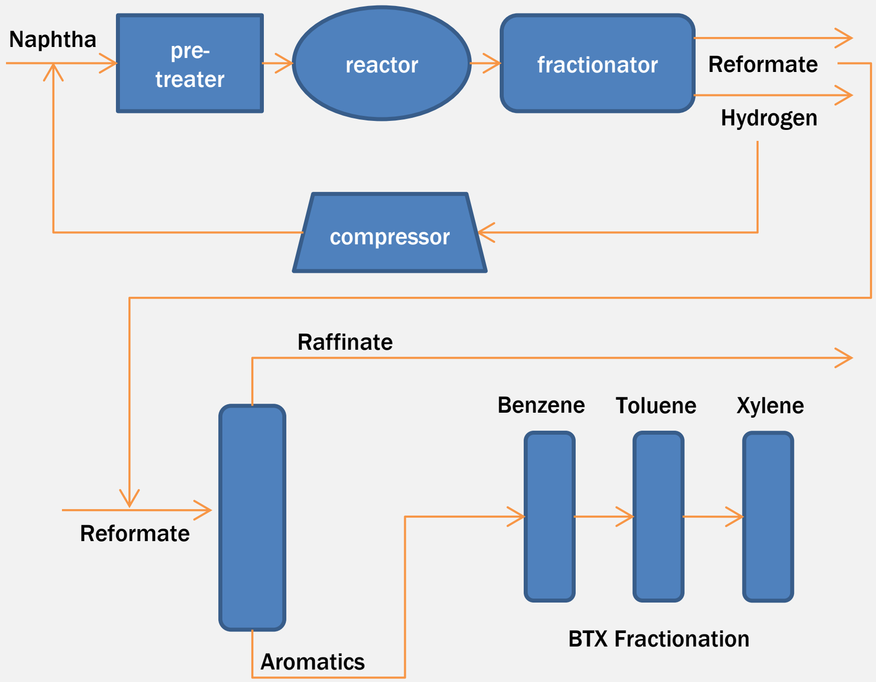
REFORMING AND BTX RECOVERY

- Heavy naphtha from CDU altered to increase octane
- Converts paraffins into naphthenes, releasing hydrogen
- Reformate is then used as a gasoline blend.
- Contains significant amounts of benzene, toluene, and xylene.
- Reformate also used as feed in BTX Recovery Unit



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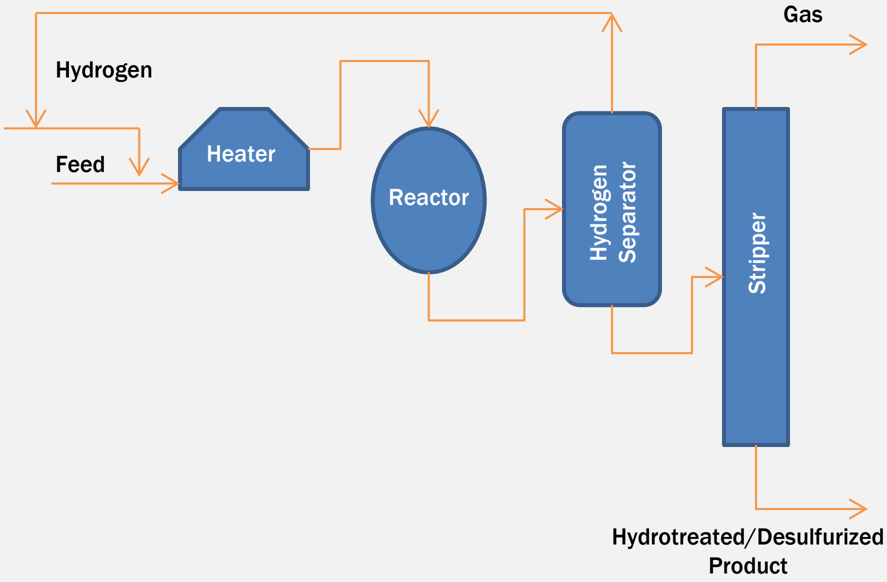
HYDROTREATING

- Process used to break sulfur away from hydrocarbon
- Stream mixed with hydrogen, heated, and charged to unit with a catalyst
- Hydrogen combines with sulfur to form H2S
- As contaminants crack away from hydrocarbon, gases form



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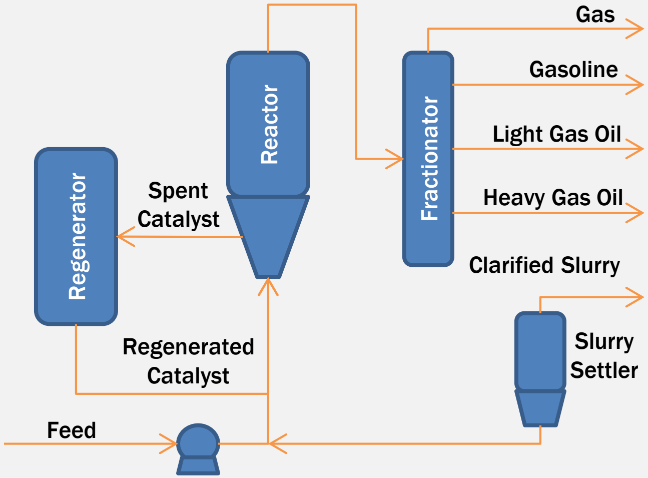
CATALYTIC CRACKING

- Primary function is to crack gas oil to produce more gasoline
- Main feedstock is Vacuum Gas Oil
- Uses a fluidized catalyst, referred to as Fluidized Catalytic Cracking Unit, FCCU or FCC
- After gas oil is cracked, effluent is processed in fractionators
- Gasoline and light gas oil are desulfurized before blending, and heavy gas oil is cracked in hydrocracker
- Bottoms are referred to as slurry or decant oil. Can be blended in RFO, processed in coker, or used as feed for carbon black.
- Produces propylene that can be used as feed to alkylation unit or can be used as petrochemical feedstock.



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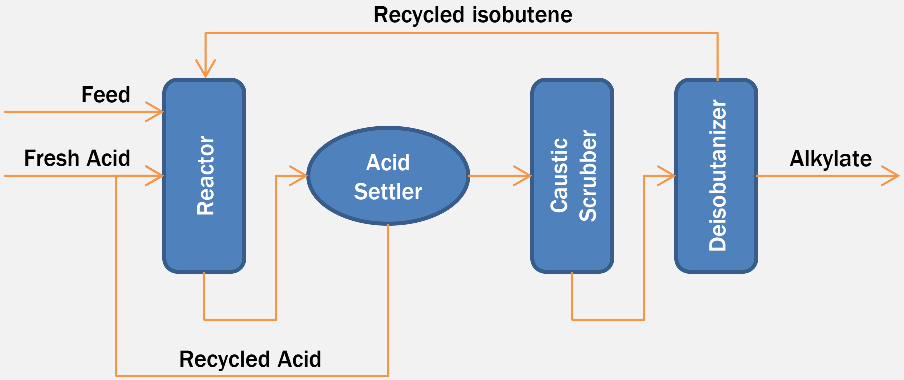
ALKYLATION

- Important source of octane for gasoline
- Reaction of propylene or butylene with isobutane to form an iso-paraffin called alkylate.
- Inverse of cracking because there is significant shrinkage
- 1bbl of propylene and 1.6 bbl of isobutane yield 2.1 bbl of alkylate
- 1bbl of butylene and 1.21 bbl of isobutane yield 1.8 bbl of alkylate.
- Either sulfuric acid or hydrofluoric acid is used as the catalyst for the reaction.



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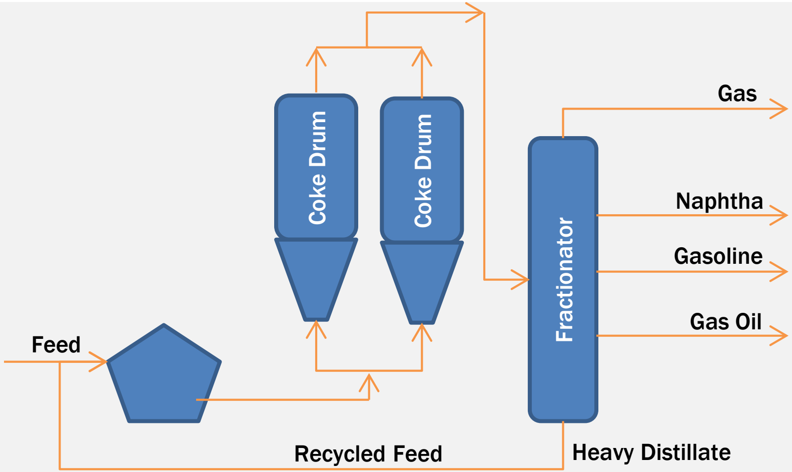
COKER

- Upgrades bottoms primarily from CDU and VDU units to higher valued products
- Coker yields gas, gasoline, distillate, and petroleum coke
- Feed is quickly heated to about 1,000°F and charged to bottom of coke drum
- Cracked product rises and drawn off, sent to fractionator
- Carbon left is coke in solid form
- Decoking is done by drillng a hole followed by high pressure water jet lowered into hole
- Coke is then railed or trucked
- Delayed cokers comes in pairs
- Higher sulfur coke is used in power generation, cement production, and steel production.
- Lower sulfur coke is used in carbon anode production for aluminum industry, TIO2 production, and recarb applications for steel production.



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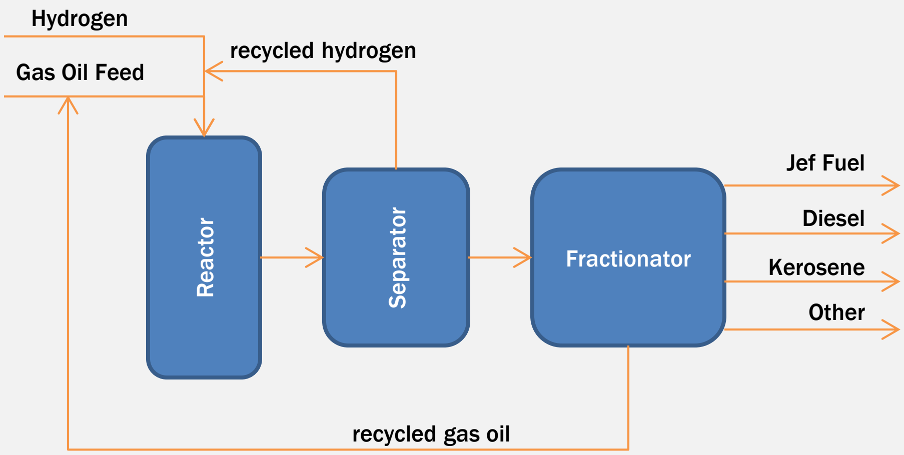
HYDROCRACKER

- Cracks low quality heavy gas oil into jet fuel, diesel, and gasoline
- Takes feed from CDU, VDU, FCC, and Coking units
- Catalytic cracking in presence of Hydrogen
- Many refiners do not have hydrocrackers, but may be incentivize to build them to increase distillate yield



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GASOLINE BLENDING

SPECS

- RVP – Reid Vapor Pressure – measure of the surface pressure it takes to keep a liquid from vaporizing.
  - Ideal RVP for gasoline varies with seasons and location
  - Blending components needed to meet RVP requirement
- Octane – measures of whether a gasoline will knock

The Octane number of any gasoline blend or blending component equals the percent of iso-octane in the iso-octane/normal heptane blend that knocks at the same compression ratio as the gasoline or component being evaluated.

- Research Octane Number (RON) test simulates driving under mild, cruising conditions
- Motor Octane Number (MON) test simulates operations under high speeds

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COMPONENTS

- iC4
- nC4
- Reformate
- Hydrocrackate
- Alkylate
- Straight-Run Gasoline
- Straight-Run Naphtha
- Cat Cracked Gasoline
- Coker Gasoline

Source: http://www.texasaromatics.com/products

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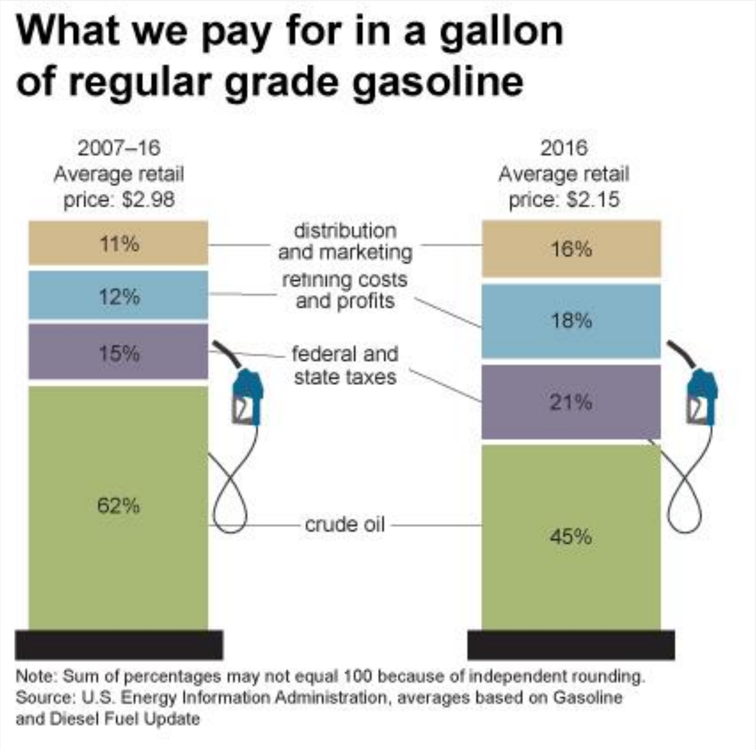
PRICE AT PUMP

- Sold based on octane levels
- Cost of crude
- Refining costs and profits
- Distribution and marketing costs and profits
- Taxes



https://www.eia.gov/petroleum/gasdiesel/

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REFINING ECONOMICS

ECONOMIC INDICATORS

- Benchmark Crudes (i.e. Brent, WTI, Dubai, LLS, WCS)
- Light Heavy Spread (i.e. LLS vs Maya)
- Refining Margin – Difference between total revenue from product sales and total costs of all crude.
- Crack Spreads
  - Single Product Crack Spreads – Difference in value between bbl of product and bbl of crude.
  - Multiple Product Crack Spreads
    - 3-2-1 Crack Spread
    - 5-3-2 Crack Spread
    - 2-1-1 Crack Spread
    - 6-3-2-1 Crack Spread
- Coker Contribution

REFINERY OPTIMIZATION

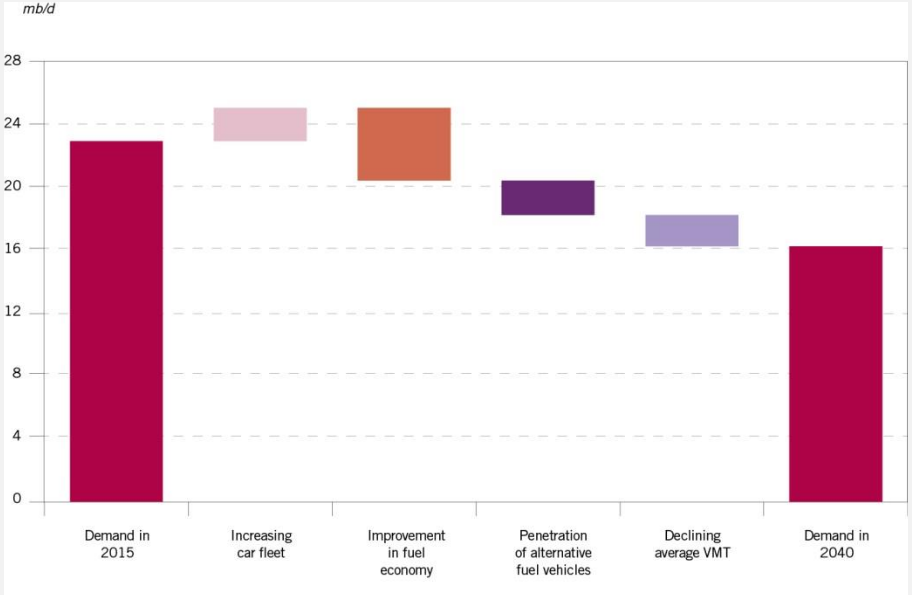
- Crude Purchasing/Selection
- Turnaround/Maintenance Planning
- Capital Investments
- Operation Schedules
  - Utilization Rates
  - Cut Points
  - Severity
- Linear Programming
  - Flexibilities
  - Constraints

FORECASTING

- Crude price relationship
- Historical Relationships (seasonality)
- GDP (long term)
- Shipping Rates (contracts, arbs, delivered price)
- Infrastructure (pipelines, terminals, rail)
- Trends (peak oil, peak demand, technologies)

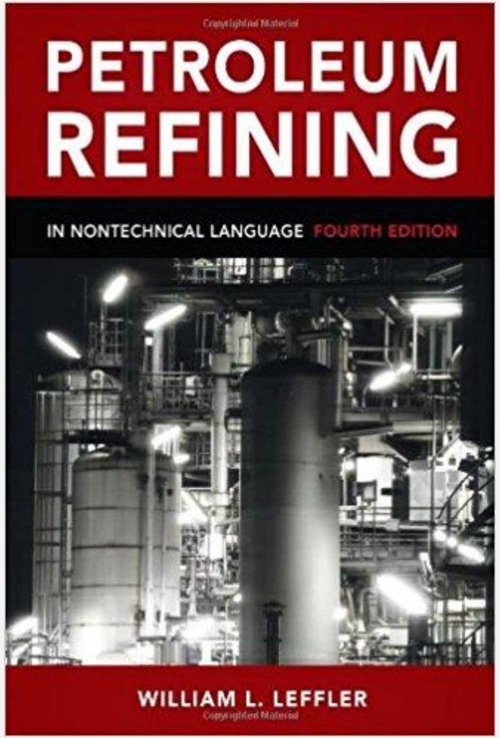
CHALLENGES

- Environmental Regulations
  - IMO MARPOL Annex VI
  - EPA Regulations
- Declining Gasoline Demand
  - Electric Vehicles
  - Autonomous Vehicles
  - Ride Sharing



https://woo.opec.org/index.php/woo-2016-figures

LITERATURE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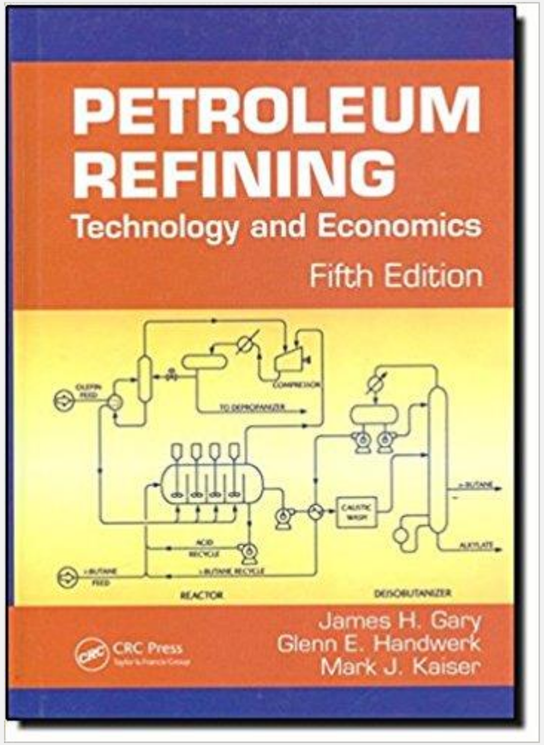
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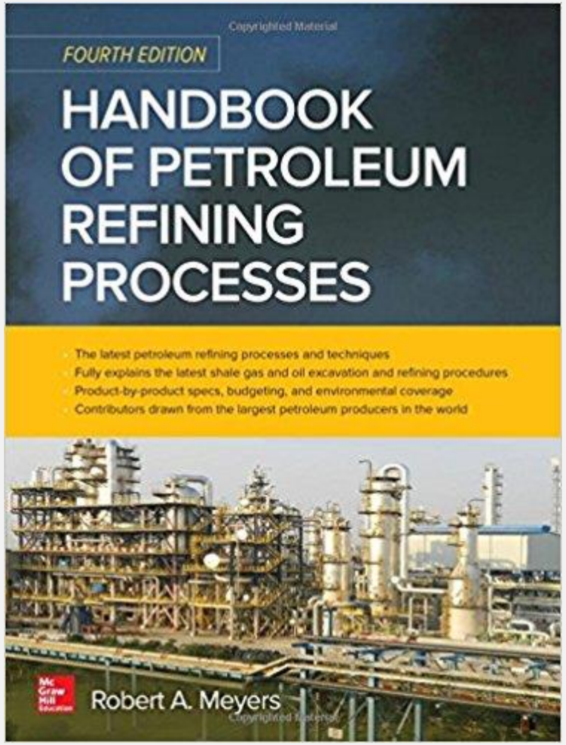
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Fully explains the latest shale gas and oil excavation and refining procedures
Product-by-product specs, budgeting, and environmental coverage
Contributors drawn from the largest petroleum producers in the world
Robert A. Meyers

Q&A

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