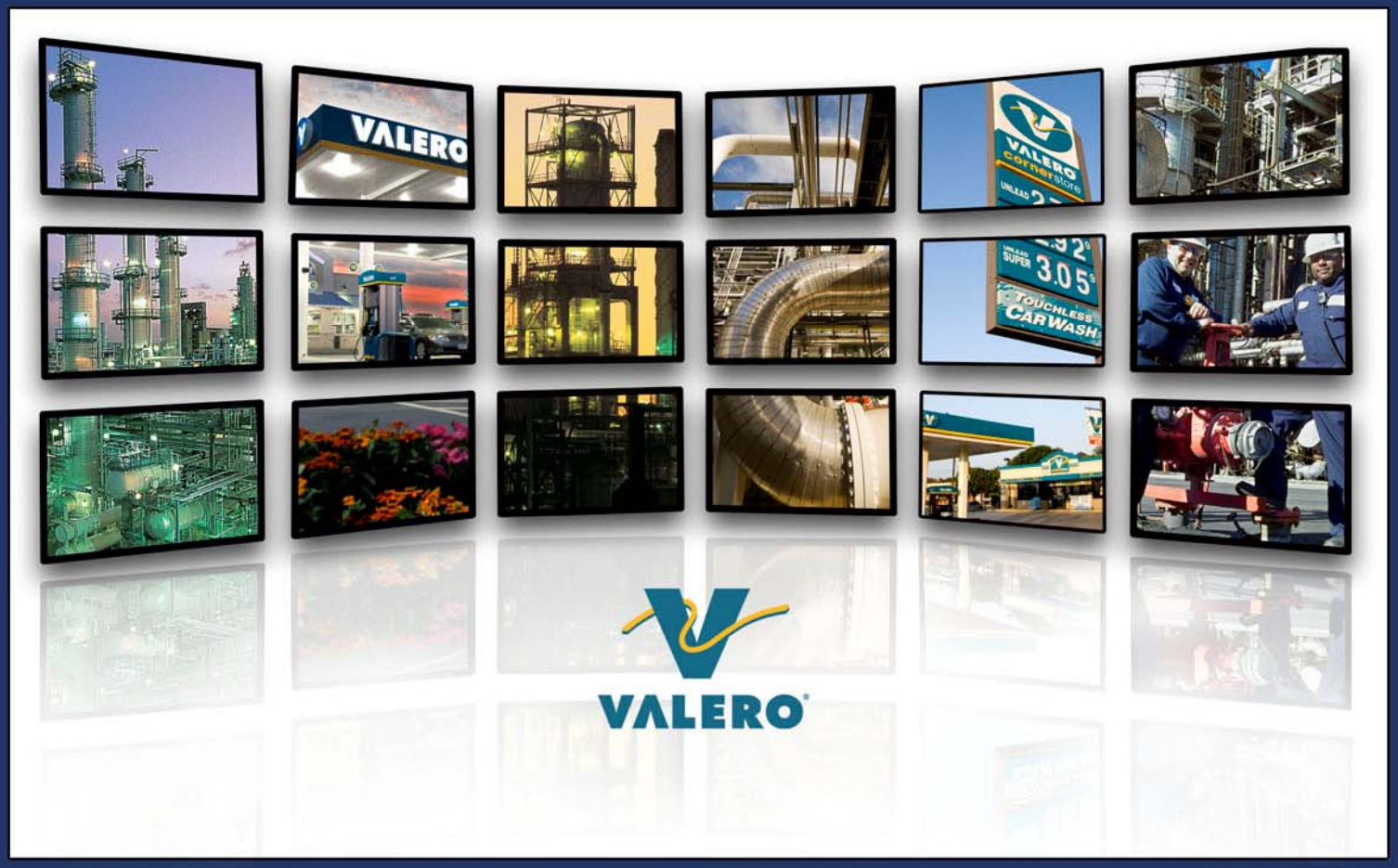
Refining 101 + Technical Teach-in on the Hydrotreater & Hydrocracker



January 13, 2009

Safe Harbor Statement

Statements contained in this presentation that state the Company's or management's expectations or predictions of the future are forward–looking statements intended to be covered by the safe harbor provisions of the Securities Act of 1933 and the Securities Exchange Act of 1934. The words "believe," "expect," "should," "estimates," and other similar expressions identify forward–looking statements. It is important to note that actual results could differ materially from those projected in such forward–looking statements. For more information concerning factors that could cause actual results to differ from those expressed or forecasted, see Valero's annual reports on Form 10-K and quarterly reports on Form 10-Q, filed with the Securities and Exchange Commission, and available on Valero's website at www.valero.com.

Rich Marcogliese

Executive Vice President

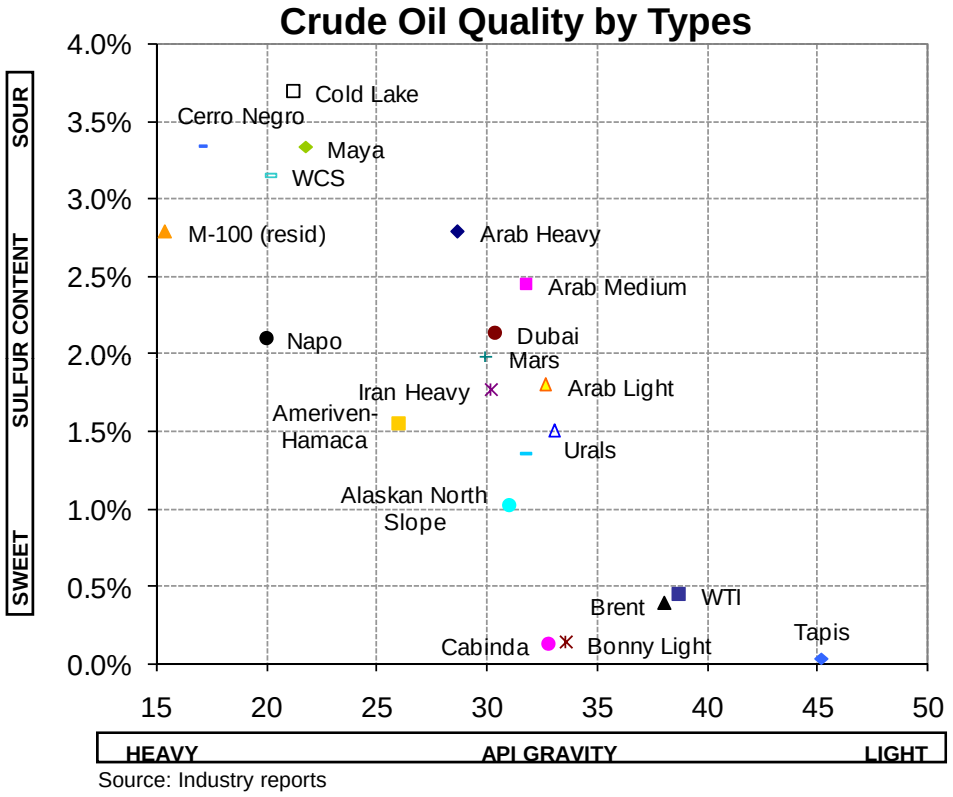
and

Chief Operating Officer

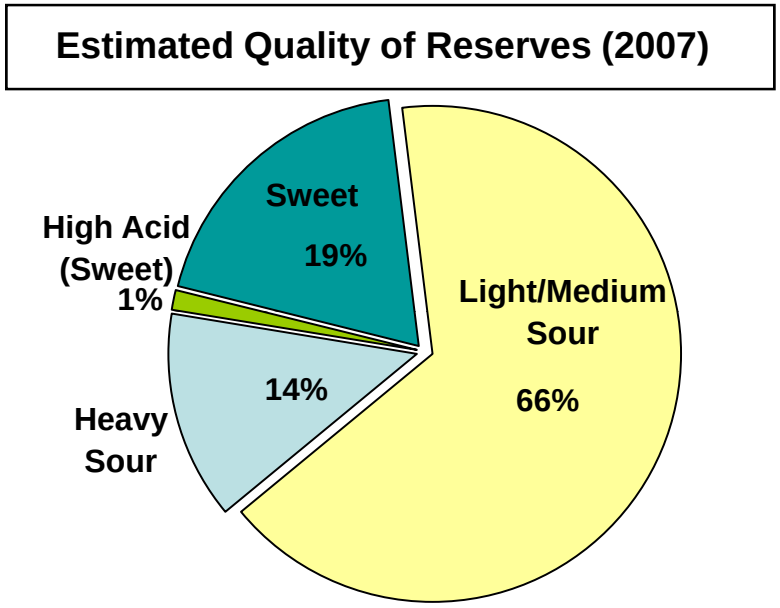
Crude Oil Characteristics

- Crudes are classified and priced by density and sulfur content
- Crude density is commonly measured by API gravity
  - API gravity provides a relative measure of crude oil density
  - The higher the API number, the lighter the crude
    - Light crudes are easier to process
    - Heavy crudes are more difficult to process
- Crude sulfur content is measured as a percentage
  - Less than 0.7% sulfur content = sweet
  - Greater than 0.7% sulfur content = sour
  - High sulfur crudes require additional processing to meet regulatory specs
- Acid content is measured by Total Acid Number (TAN)
  - Acidic crudes highly corrosive to refinery equipment
  - High acid crudes are those with TAN greater than 0.7

Crude Oil Basics



Source: Industry reports



Source: DOE, Oil & Gas Journal, Company Information

- **Majority of global crude oil reserves are sour**
- **Most quoted benchmark prices are light sweet crude oils**
  - WTI (West Texas Intermediate), Western Hemisphere
  - Brent (North Sea Crude), Europe

What's in a Barrel of Crude Oil?

Crude Oil Types	Characteristics	Inherent Yields
Light Sweet (e.g. WTI, LLS, Brent)	> 34 API Gravity < 0.7 % Sulfur 35% Demand Most Expensive	3% / 32% / 30% / 35%
Medium Sour (e.g. Mars, Arab Light, Arab Medium, Urals)	24 to 34 API Gravity > 0.7 % Sulfur 50% Demand Less Expensive	2% / 24% / 26% / 48%
Heavy Sour (e.g. Maya, Cerro Negro, Cold Lake, Western Canadian Select)	< 24 API Gravity > 0.7 % Sulfur 15% Demand Least Expensive	1% / 15% / 21% / 63%

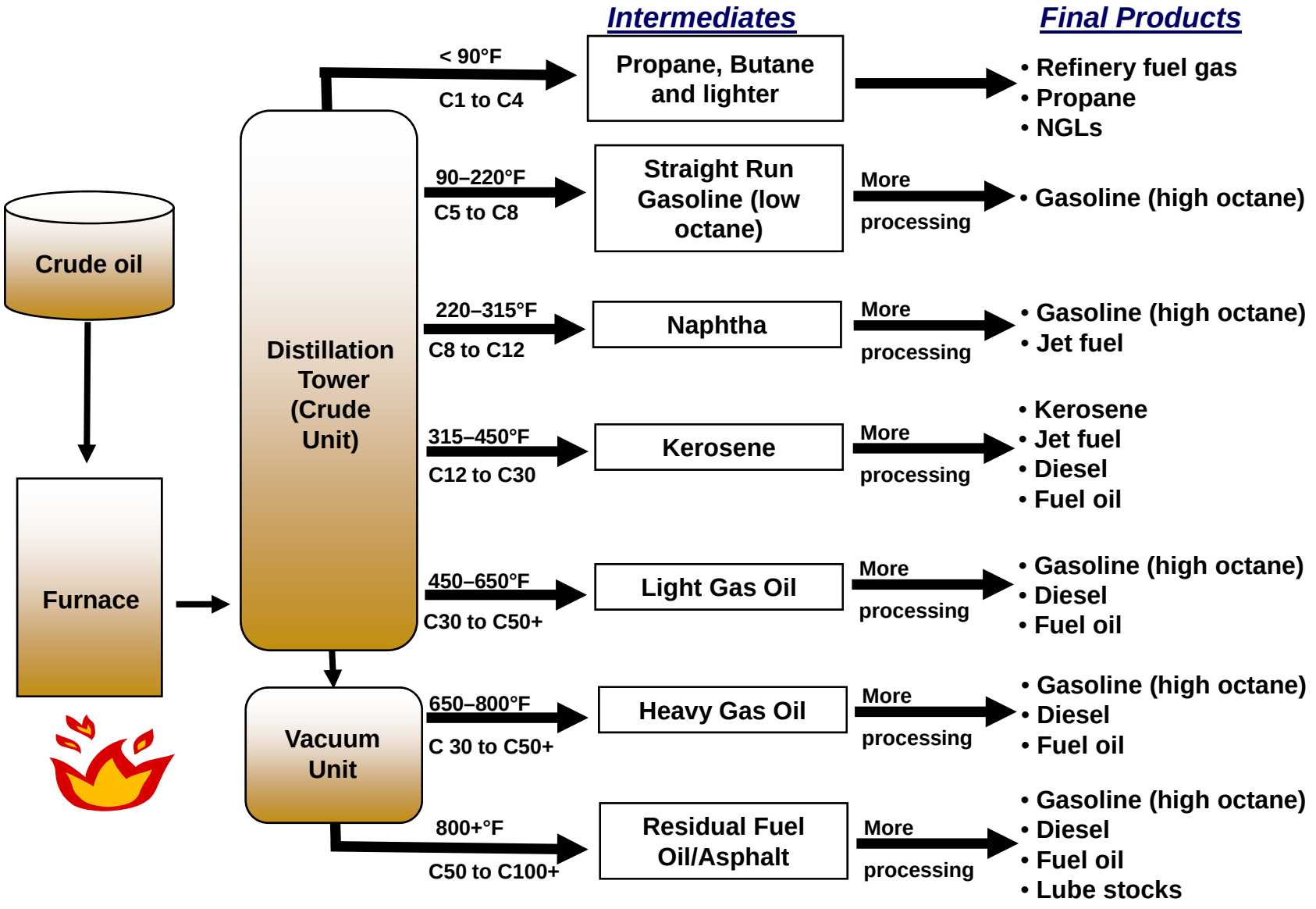
2007 U.S. Refinery Production

8%	Refinery Gases
48%	Gasoline RFG Conventional CARB Premium
35%	Distillate Jet Fuel Diesel Heating Oil
9%	Heavy Fuel Oil & Other

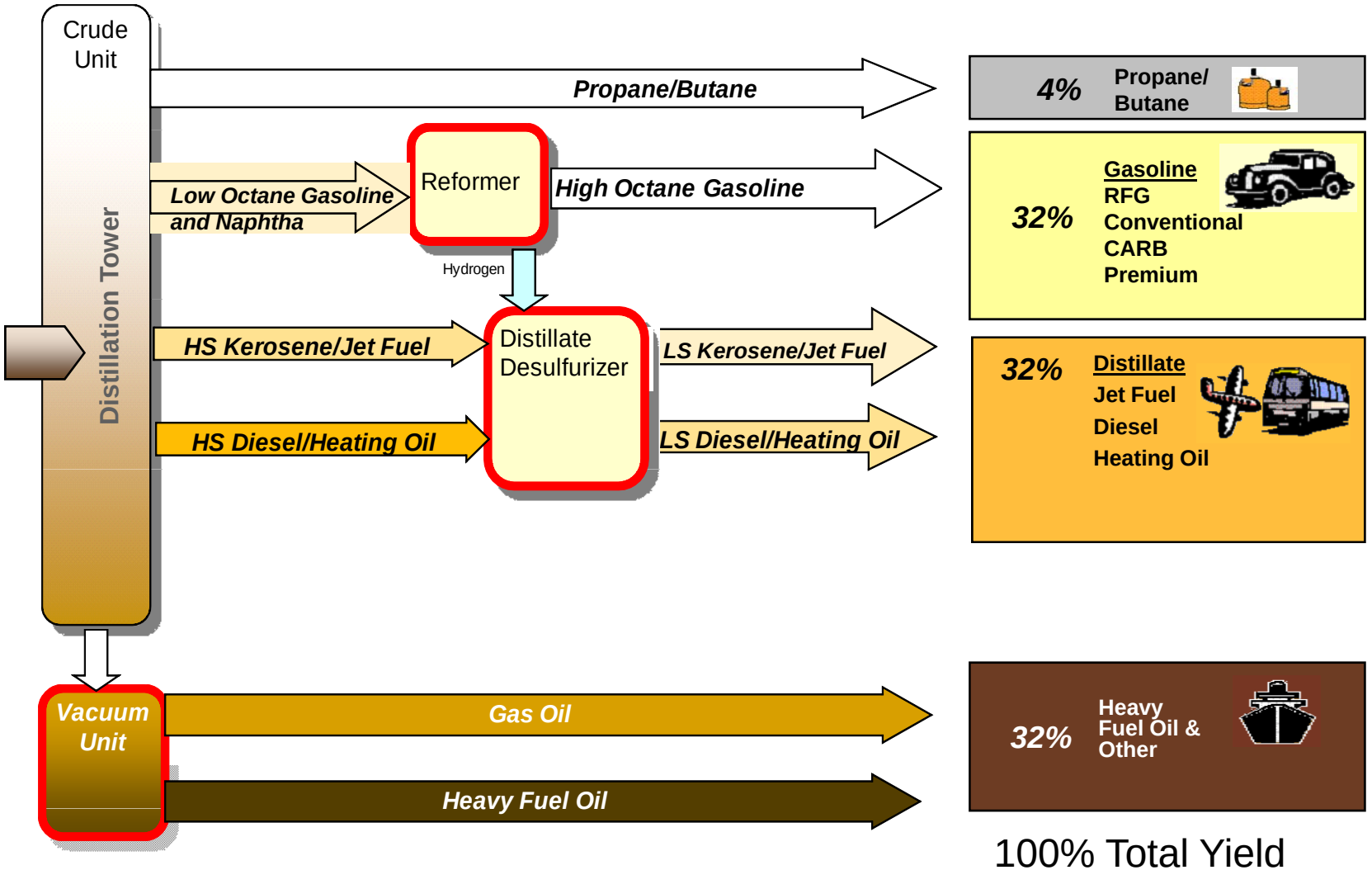
Source: EIA Refiner Production

Refineries upgrade crude oil to higher value products

Basic Refining Concepts



Hydroskimming/Topping Refinery



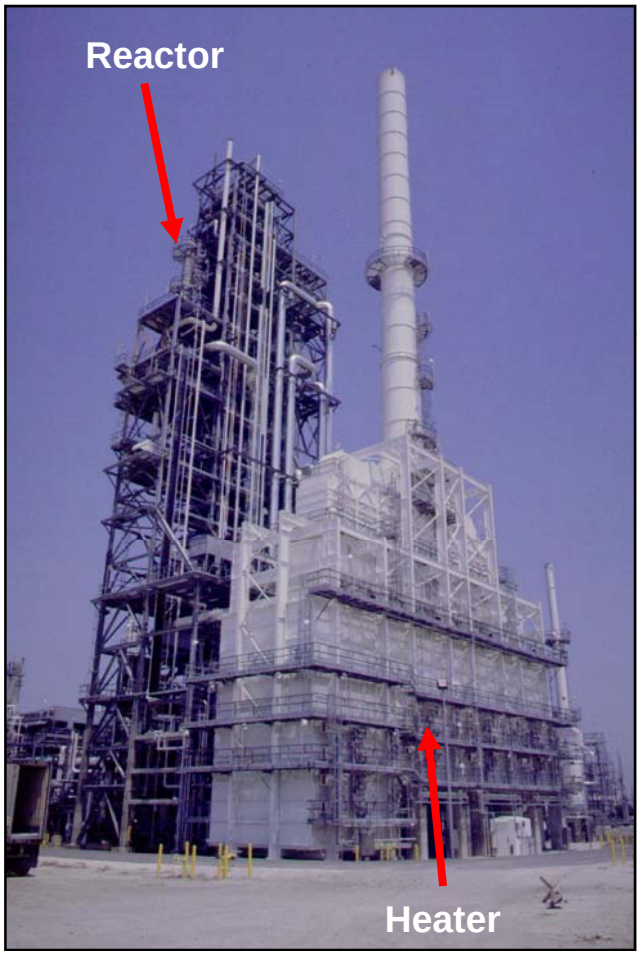
100% Total Yield

Simple, low upgrading capability refineries run sweet crude

Crude and Vacuum Towers

Crude Atmospheric Tower

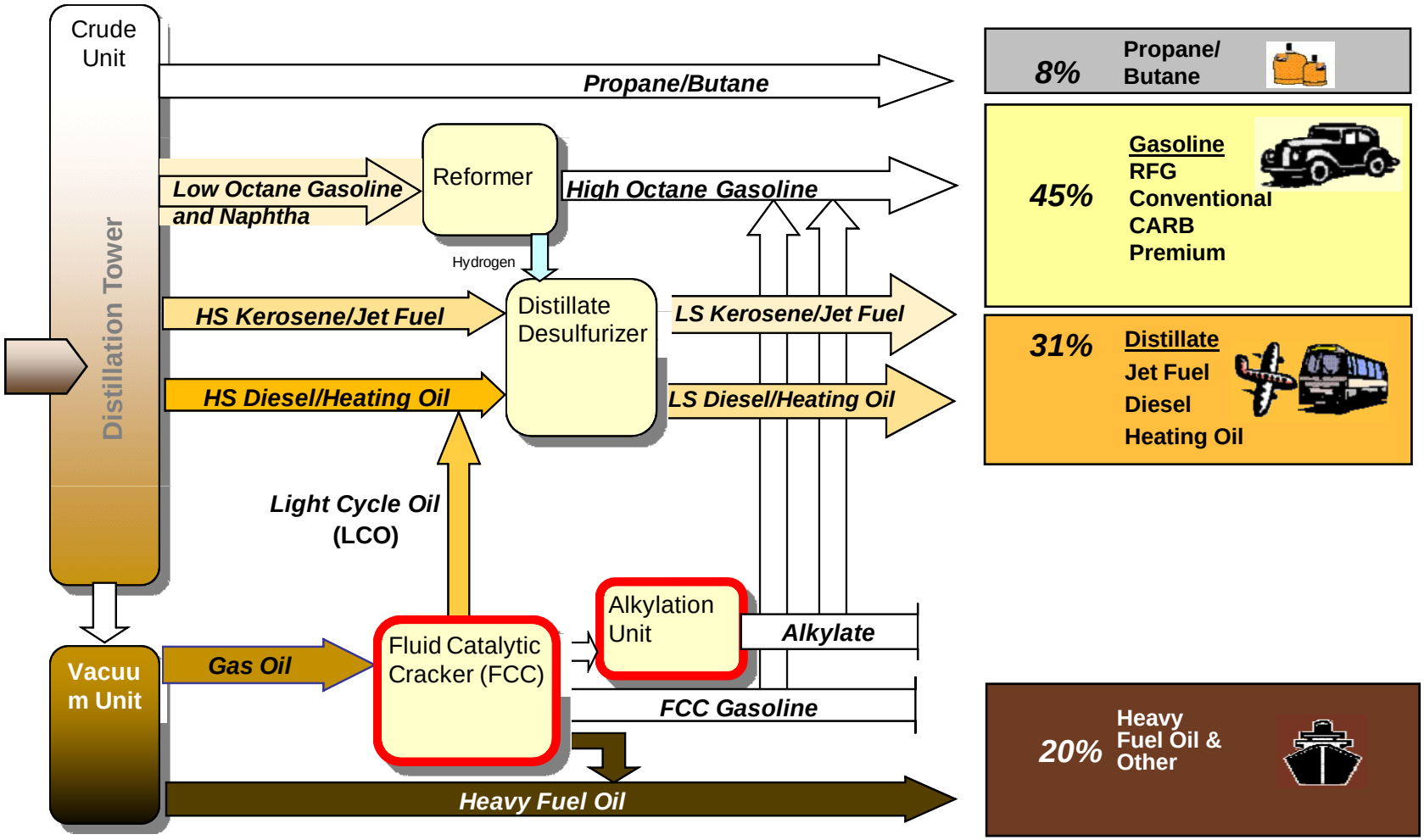
Vacuum Tower



Reformer

Medium Conversion: Catalytic Cracking

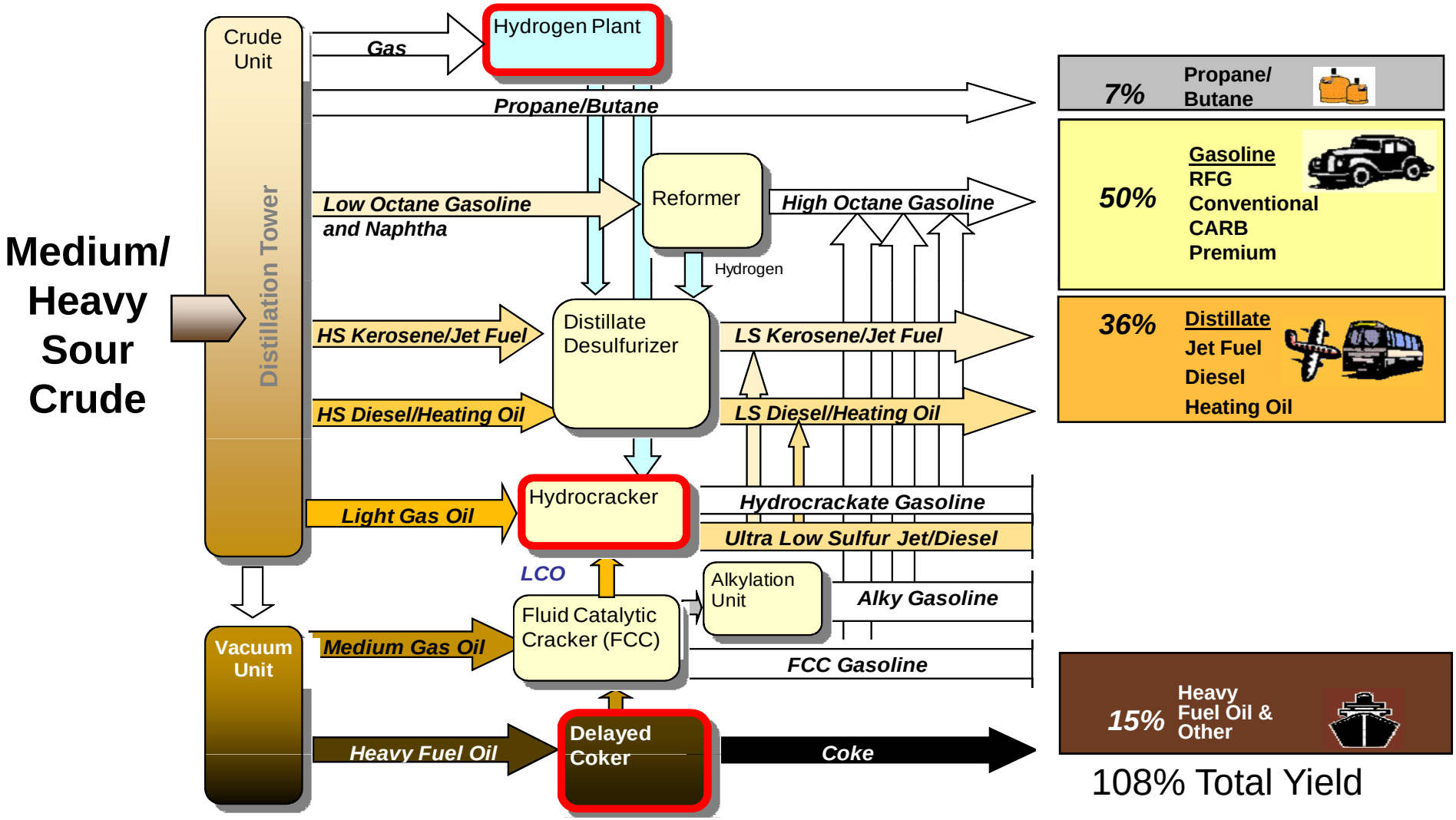
Light Sour Crude



104% Total Yield

Moderate upgrading capability refineries tend to run more sour crudes while achieving increased higher value product yields and volume gain

High Conversion: Coking/Resid Destruction



Complex refineries can run heavier and more sour crudes while achieving the highest light product yields and volume gain

FCC and Hydrocracker Reactors

Fluidized Catalytic Cracker

Hydrocracker Reactors

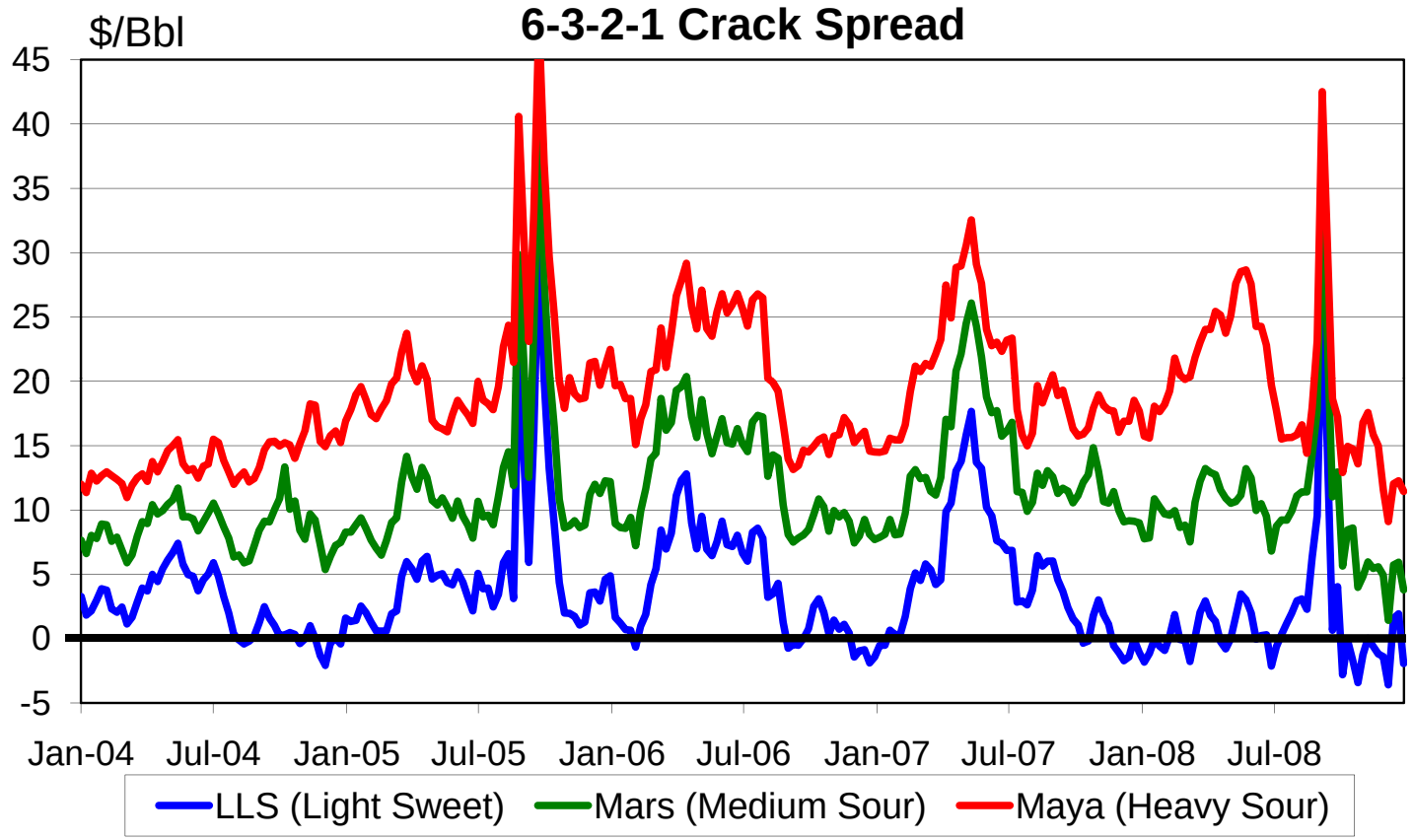
Cokers

Delayed Coker

Superstructure holds the drill and drill stem while the coke is forming in the drum

Fluid Coker

Conversion Economics

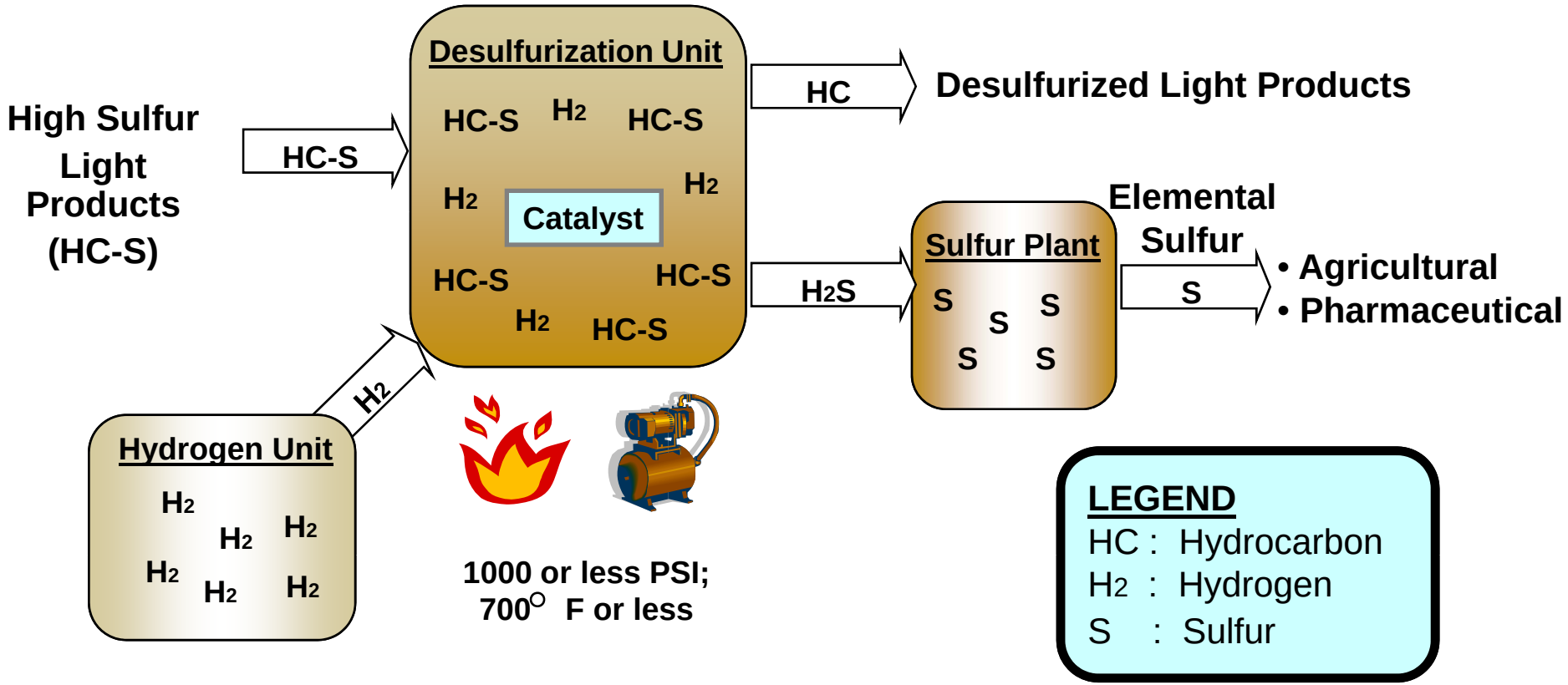


- **Need conversion capacity to capitalize on sour crude oil differentials**
  - Hydroskimming – Breakeven or moderate margins; High resid yield
    - When margins are positive – increase crude oil runs
    - When margins are negative – decrease crude oil runs
  - Cracking – Better margins; Lower resid yield
  - Coking – Best margins; Lowest resid yield
    - Maximize heavy crude oils

Desulfurization Basics

Objective

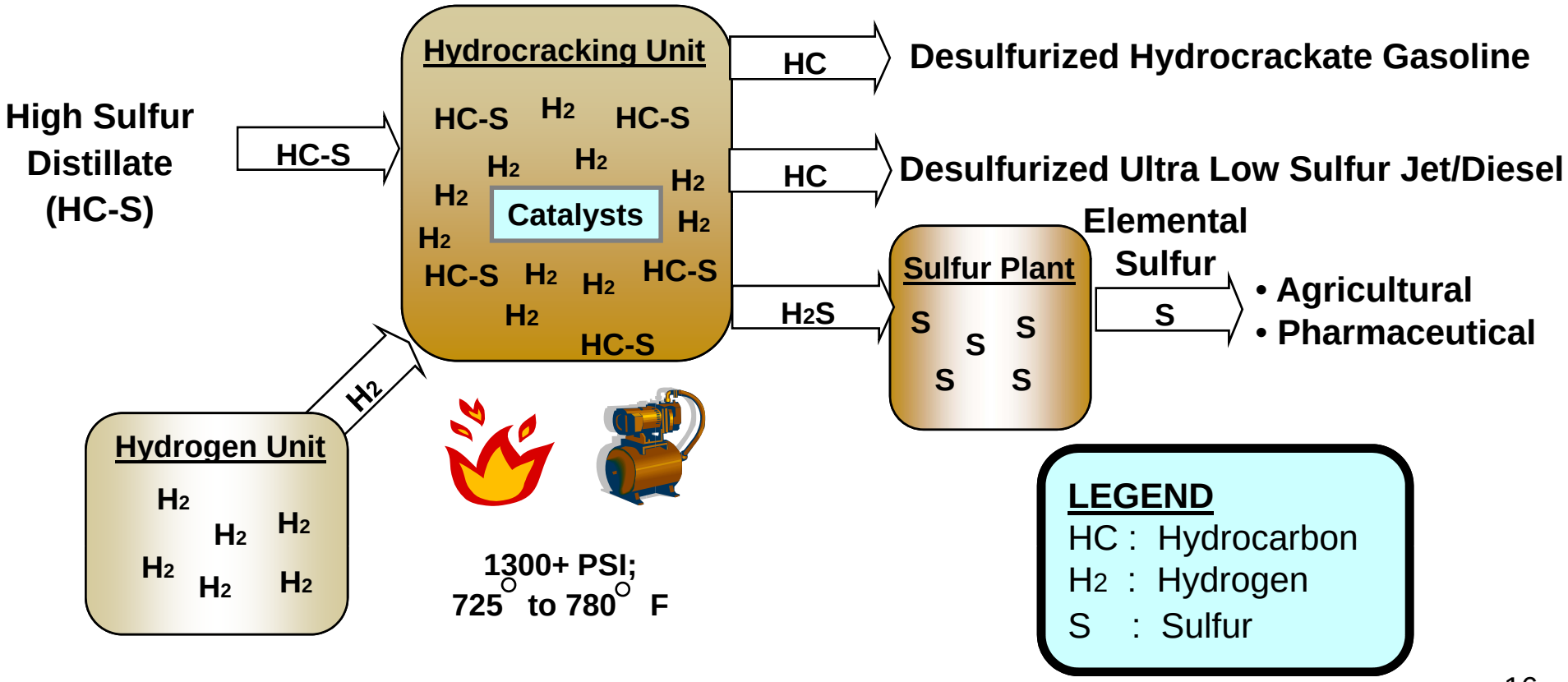
- Remove sulfur from light products (gasoline or diesel) to meet air quality requirements for clean burning fuels
- Units are called desulfurization or hydrotreater



Hydrocracking Basics

Objective

- Value added upgrading of high sulfur distillates to low sulfur gasoline and ultra low sulfur jet/diesel to meet air quality requirements for clean burning fuels
- Typically achieve 20% to 25% volume expansion due to hydrogen saturation



Hydrocrackers

McKee Hydrocracker

Corpus Christi Hydrocracker

Distillate Yield Maximization

- Recent economics have incentivized maximization of distillate rather than gasoline
- Typical opportunities to increase distillate yields
  - Immediate, non-capital opportunities — +2 to 4%
    - Examples: Optimization of distillation cut points, re-routing of intermediate streams, and tank optimization
  - Non-capital taking < 1yr — +1 to 2%
    - Examples: FCC catalyst change, HCU catalyst selection
  - Capital projects taking < 1 yr — +1 to 2%
    - Examples: Minor hardware changes (tower internals, reactor distributors, ect.), hydraulic debottlenecking
  - Capital projects taking > 1 year — +3 to 5%
    - Examples: Install/expand distillate draw capacity on fractionators, additional fractionation, new HCU

Total +7 to 13%

Q & A

Appendix

Major Refining Processes – Crude Processing

- **Definition**
  - Separating crude oil into different hydrocarbon groups
  - The most common means is through distillation
- **Process**
  - Desalting – Prior to distillation, crude oil is often desalted to remove corrosive salts as well as metals and other suspended solids.
  - Atmospheric Distillation – Used to separate the desalted crude into specific hydrocarbon groups (straight run gasoline, naphtha, light gas oil, etc.) or fractions.
  - Vacuum Distillation – Heavy crude residue ("bottoms") from the atmospheric column is further separated using a lower–pressure distillation process. Means to lower the boiling points of the fractions and permit separation at lower temperatures, without decomposition and excessive coke formation.

Major Refining Processes – Cracking

- **Definition**
  - "Cracking" or breaking down large, heavy hydrocarbon molecules into smaller hydrocarbon molecules thru application of heat (thermal) or through the use of catalysts
- **Process**
  - Coking – Thermal non–catalytic cracking process that converts low value oils to higher value gasoline, gas oils and marketable coke. Residual fuel oil from vacuum distillation column is typical feedstock.
  - Visbreaking – Thermal non–catalytic process used to convert large hydrocarbon molecules in heavy feedstocks to lighter products such as fuel gas, gasoline, naphtha and gas oil. Produces sufficient middle distillates to reduce the viscosity of the heavy feed.
  - Catalytic Cracking – A central process in refining where heavy gas oil range feeds are subjected to heat in the presence of catalyst and large molecules crack into smaller molecules in the gasoline and surrounding ranges.
  - Catalytic Hydrocracking – Like cracking, used to produce blending stocks for gasoline and other fuels from heavy feedstocks. Introduction of hydrogen in addition to a catalyst allows the cracking reaction to proceed at lower temperatures than in catalytic cracking, although pressures are much higher.

Major Refining Processes – Combination

- **Definition**
  - Linking two or more hydrocarbon molecules together to form a large molecule (e.g. converting gases to liquids) or rearranging to improve the quality of the molecule
- **Process**
  - Alkylation – Important process to upgrade light olefins to high–value gasoline components. Used to combine small molecules into large molecules to produce a higher octane product for blending with gasoline.
  - Catalytic Reforming – The process whereby naphthas are changed chemically to increase their octane numbers. Octane numbers are measures of whether a gasoline will knock in an engine. The higher the octane number, the more resistance to pre or self–ignition.
  - Polymerization – Process that combines smaller molecules to produce high octane blending stock.
  - Isomerization – Process used to produce compounds with high octane for blending into the gasoline pool. Also used to produce isobutene, an important feedstock for alkylation.

Major Refining Processes – Treating

- **Definition**
  - Processing of petroleum products to remove some of the sulfur, nitrogen, heavy metals, and other impurities
- **Process**
  - Catalytic Hydrotreating, Hydroprocessing, sulfur/metals removal – Used to remove impurities (e.g. sulfur, nitrogen, oxygen and halides) from petroleum fractions. Hydrotreating further "upgrades" heavy feeds by converting olefins and diolefins to parafins, which reduces gum formation in fuels. Hydroprocessing also cracks heavier products to lighter, more saleable products.

List of Refining Acronyms

- AGO – Atmospheric Gas Oil
- ATB – Atmospheric Tower Bottoms
- B–B – Butane–Butylene Fraction
- BBLS – Barrels
- BPD – Barrels Per Day
- BTX – Benzene, Toluene, Xylene
- CARB – California Air Resource Board
- CCR – Continuous Catalytic Regenerator
- DAO – De–Asphalted Oil
- DCS – Distributed Control Systems
- DHT – Diesel Hydrotreater
- DSU – Desulfurization Unit
- EPA – Environmental Protection Agency
- ESP – Electrostatic Precipitator
- FCC – Fluid Catalytic Cracker
- GDU – Gasoline Desulfurization Unit
- GHT – Gasoline Hydrotreater
- GOHT – Gas Oil Hydrotreater
- GPM – Gallon Per Minute
- HAGO – Heavy Atmospheric Gas Oil
- HCU – Hydrocracker Unit
- HDS – Hydrodesulfurization
- HDT – Hydrotreating
- HGO – Heavy Gas Oil
- HOC – Heavy Oil Cracker (FCC)
- H2 – Hydrogen
- H2S – Hydrogen Sulfide
- HF – Hydroflouric (acid)
- HVGO – Heavy Vacuum Gas Oil
- kV – Kilovolt
- kVA – Kilovolt Amp
- LCO – Light Cycle Oil
- LGO – Light Gas Oil
- LPG – Liquefied Petroleum Gas
- LSD – Low Sulfur Diesel
- LSR – Light Straight Run (Gasoline)
- MON – Motor Octane Number
- MTBE – Methyl Tertiary–Butyl Ether
- MW – Megawatt
- NGL – Natural Gas Liquids
- NO_X – Nitrogen Oxides
- P–P – Propane–Propylene
- PSI – Pounds per Square Inch
- RBOB – Reformulated Blendstock for Oxygen Blending
- RDS – Resid Desulfurization
- RFG – Reformulated Gasoline
- RON – Research Octane Number
- RVP – Reid Vapor Pressure
- SMR – Steam Methane Reformer (Hydrogen Plant)
- SO_X – Sulfur Oxides
- SRU – Sulfur Recovery Unit
- TAME – Tertiary Amyl Methyl Ether
- TAN – Total Acid Number
- ULSD – Ultra–low Sulfur Diesel
- VGO – Vacuum Gas Oil
- VOC – Volatile Organic Compound
- VPP – Voluntary Protection Program
- VTB – Vacuum Tower Bottoms
- WTI – West Texas Intermediate
- WWTP – Waste Water Treatment Plant