

**The National Air
Compliance Training
Program**



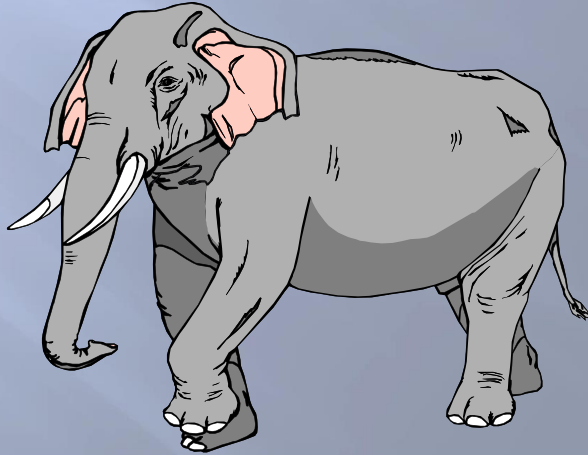
**Course 288
Petroleum Refining**
2017

Course Objectives

- Familiarize with refinery:
 - terminology
 - process
 - process equipment
- Identify:
 - air emissions sources
 - inspection points
 - regulations

How do you eat an Elephant?

One bite at a time.

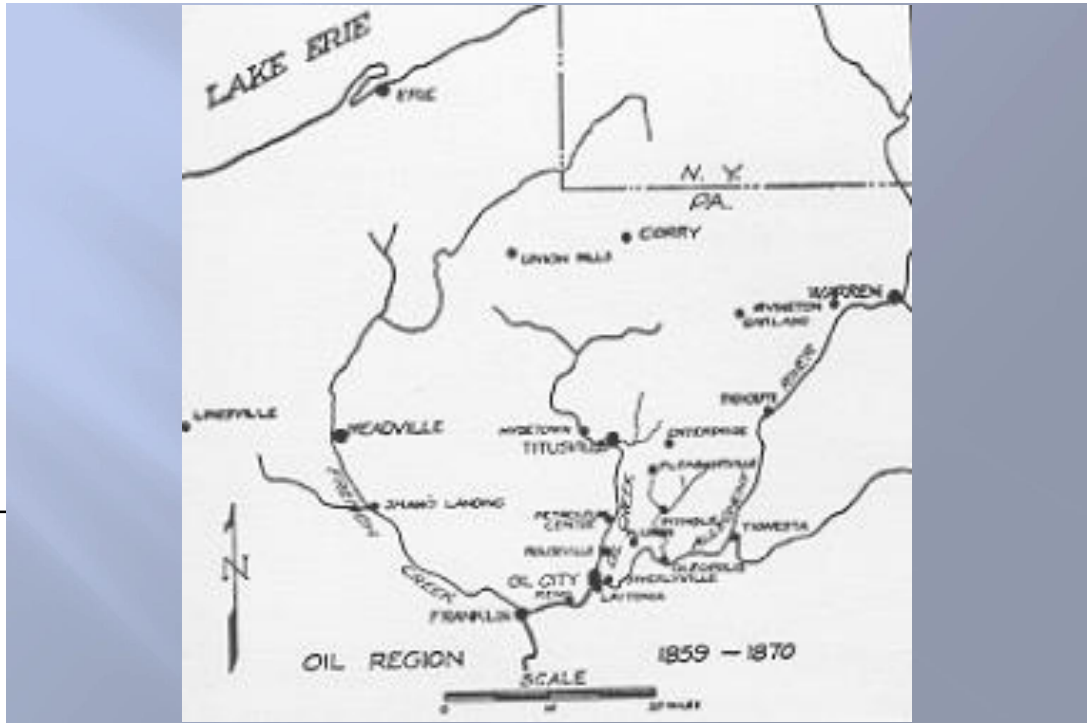


Early Uses of Petroleum

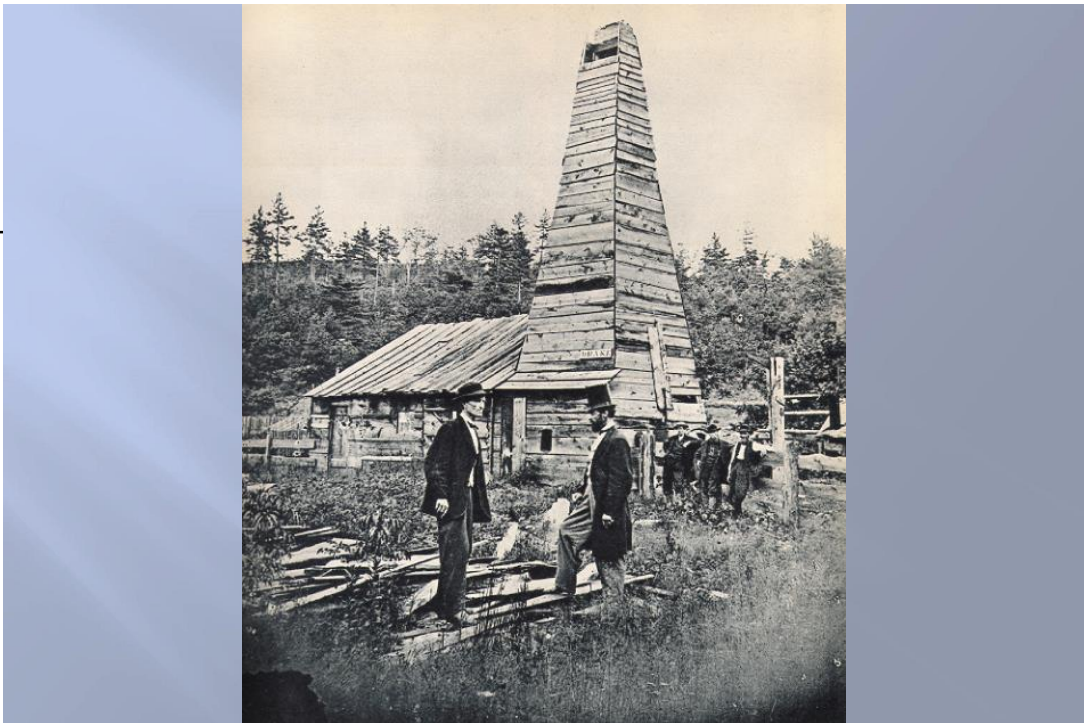
- Water Repellent and Caulking
- Grease and Lubricants
- Lamp Oil
- Medicines



Refinery Class

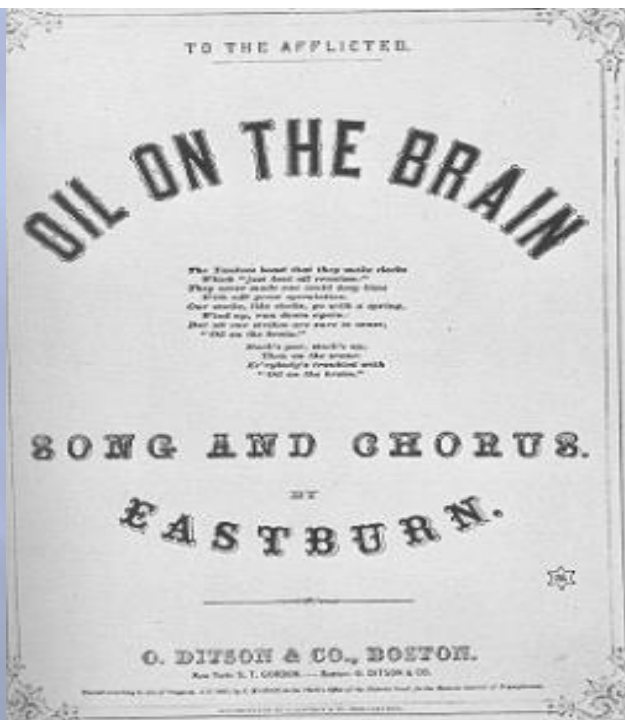


Refinery Class

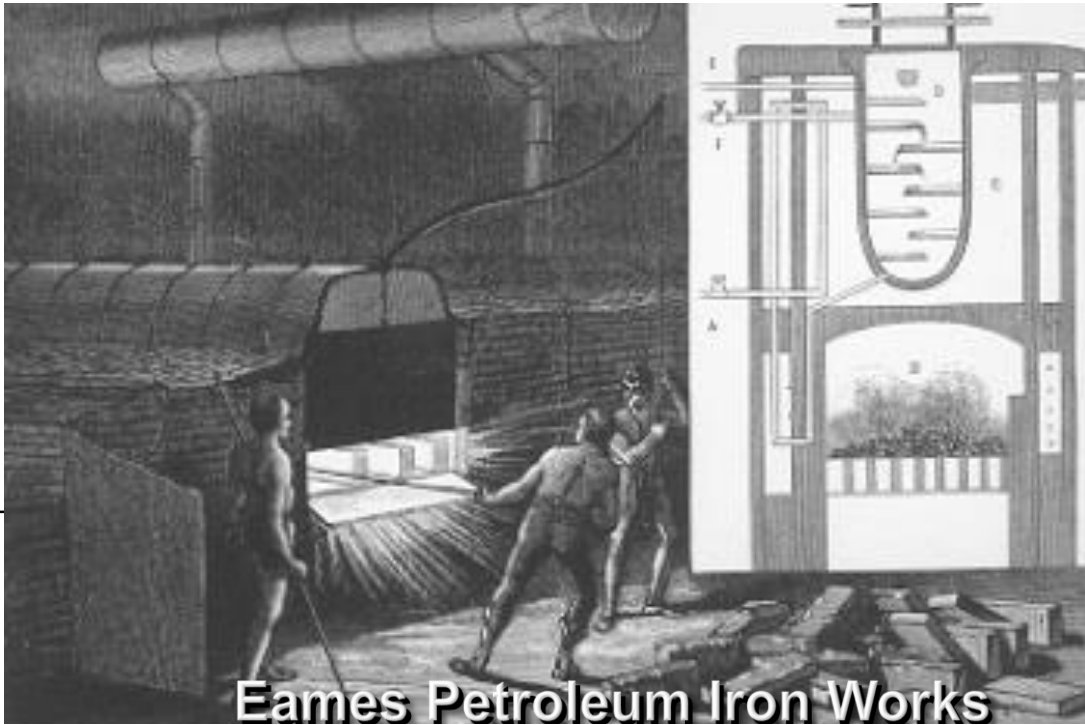


The Oil Boom

1859 was to oil as 1849 was to gold. But what to do with all of the oil?



Refinery Class



Eames Petroleum Iron Works

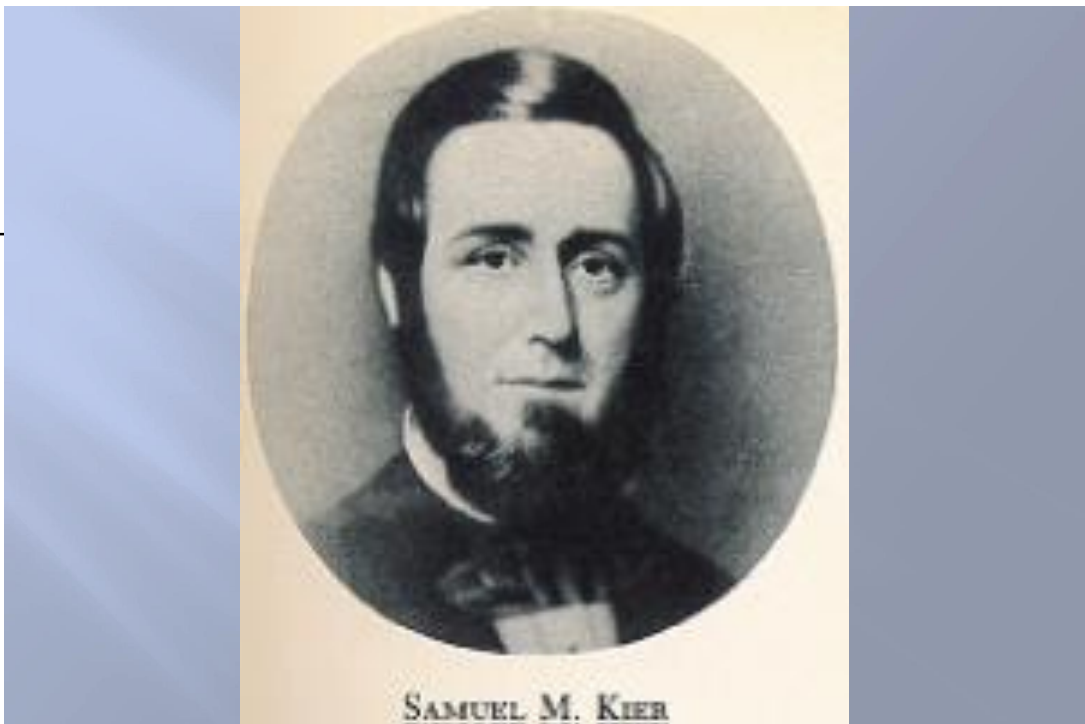
PETROLEUM, OR ROCK OIL.
A NATURAL REMEDY!
 PROCURED FROM A WELL IN ALLEGHENY COUNTY, PA.
 Four hundred feet below the Earth's Surface!
 PUT UP AND SOLD BY
SAMUEL M. KIRK,
 CANAL BASIN, SEVENTH STREET, PITTSBURGH, PA.

The beneficial issue from Russia's sweet spring,
 The bloom of health, and life, to men will bring,
 As from her depths the mighty liquid flows,
 To cure our aches, and soothe our woes.

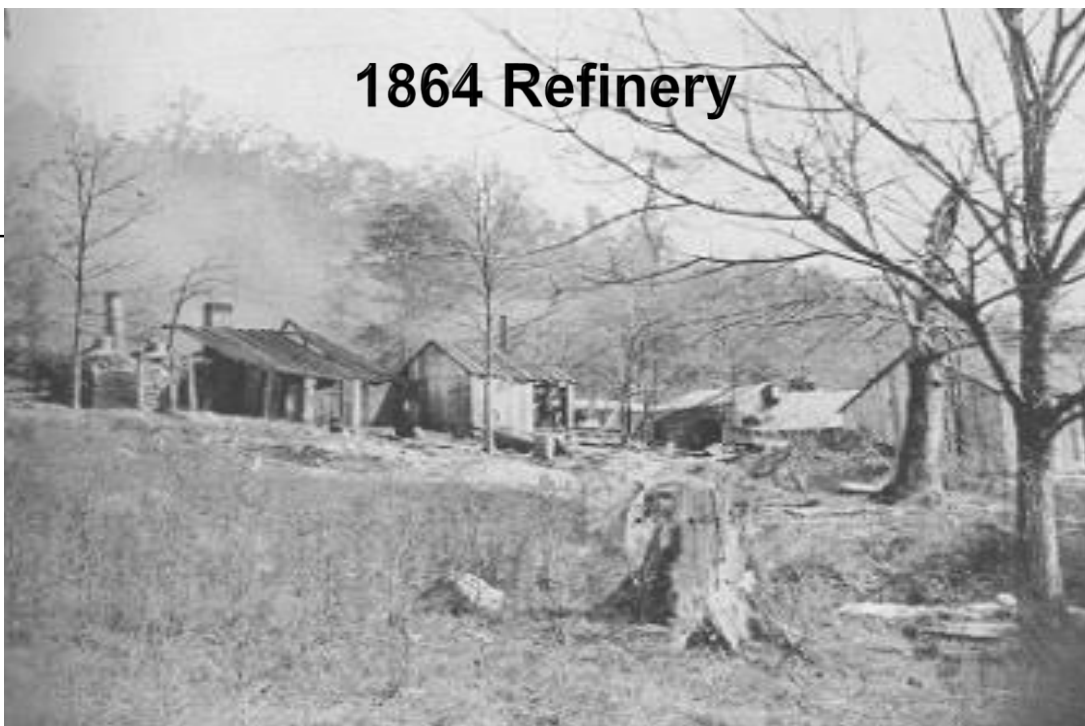
CAUTION—As many persons are now going about and vending an article of a spurious character, calling it Petroleum, or Rock Oil, we would caution the public against all preparations bearing that name not having the name of S. M. Kirk written on the label of the bottle.

PETROLEUM.—It is necessary, upon the introduction of a new medicine to the notice of the public, that something should be said in relation to its powers in healing disease, and the manner in which it acts. Man's organization is a complicated one; and to understand the functions of each organ, requires the study of years. But to understand that certain remedies produce certain impressions upon these organs, may be learned by experience in a short time. It is by observation in watching the effects of various medicines, that we are enabled to increase the number of curative agents; and when we have discovered a new medicine and ascertained its merits, it is our duty to bring it before the public, so that the benefits so to be derived from it may be more generally diffused, but have no right to hold back a remedy whose powers are calculated to remove pain and to alleviate human suffering and disease. **THE PETROLEUM HAS BEEN FULLY TESTED!** About one year ago, it was placed before the public as **A REMEDY OF WONDERFUL EFFICACY.** Every one not acquainted with its virtues, doubted its healing properties. The cry of harking was raised against it. It had some friends,—those that were cured through its wonderful agency. These speak out in its favor. The lame, through its instrumentality, were made to walk—the blind, to see. Those who had suffered for years under the torturing pains of **RHEUMATISM, GOUT, AND NEURALGIA,** were restored to health and usefulness. Several who were blind have been made to see, the evidence of which will be placed before you. If you still have doubts, go and ask those who have been cured! Some of them live in our midst, and can answer for themselves. In writing about a medicine, we are aware that we should write **TRUTH**—that we should make no statements that cannot be proved. We have the witnesses—crowds of them, who will testify in terms stronger than we can write them to the efficacy of this Remedy, who will testify that the Petroleum has done for them what no medicine ever could before—cases that were pronounced hopeless, and beyond the reach of remedial means—cases abandoned by Physicians of unquestioned celebrity, have been made to exclaim, **"THIS IS THE MOST WONDERFUL REMEDY EVER DISCOVERED!"** We will let before you the certificates of some of the most remarkable cases, to give them all, would require more space than would be allowed by this circular. Since the introduction of the Petroleum, about one year ago, many Physicians have been convinced of its efficacy, and now recommend it in their practice, and we have no doubt that in another year it will stand at the head of the list of valuable Remedies. If the Physicians do not recommend it, the people will have it of themselves—but its innocent power is lost, and good must become known and appreciated—when the voices of the cured speak out, when the same themselves stand out in bold relief, and when he who for years has suffered with the tortures and pangs of an insupportable pain, that has been shortening his days, and hastening his end, the narrow lanes appointed for all the living, when he speaks out in its praise, who will doubt it? **THE PETROLEUM IS A NATURAL REMEDY**—it is put up as it flows from the bosom of the earth, without anything being added to or taken from it.

Refinery Class



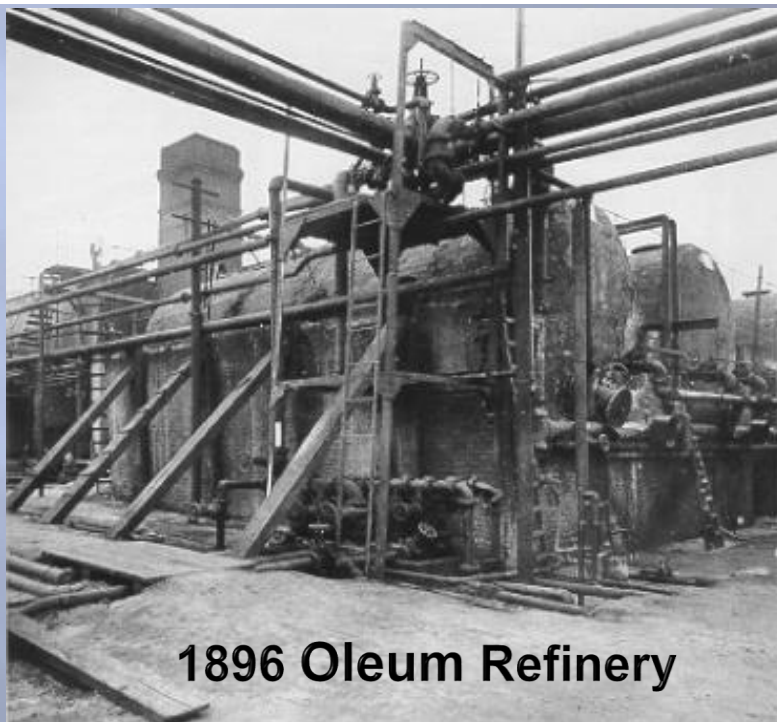
SAMUEL M. KIER



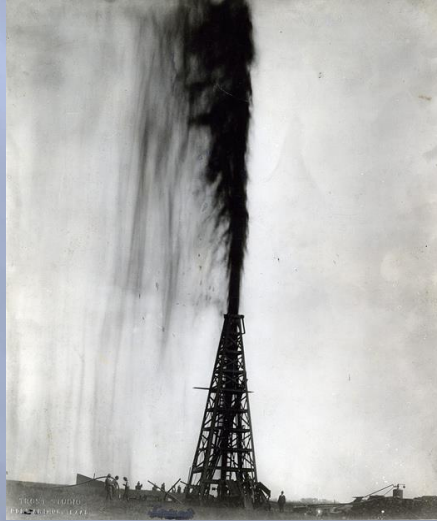
1880 Oil Refinery



1896 Oleum Refinery



Gushers



Early Refining



Top US Refineries

1. Port Arthur Refinery (Montiva), Port Arthur, TX, 600,250 Bbl/day
2. Baytown Refinery (ExxonMobil), Baytown, Texas, 584,000 Bbl/day
3. Garyville Refinery (Marathon), Garyville, LA, 522,000 bbl/day
4. Baton Rouge Refinery (ExxonMobil), Baton Rouge, LA, 503,000 Bbl/day
5. Hovensa LLC (Hovensa LLC), Kingshill, Virgin Islands, 500,000 Bbl/day
6. BP (BP), Texas City, TX, 460,000 Bbl/day
7. Lake Charles Refinery (Citgo), Lake Charles, LA, 427,800 Bbl/day
8. BP (BP), Whiting, IN, 399,000 Bbl/day
9. ExxonMobil (Exxon Mobil), Beaumont, TX, 344,500 Bbl/day
10. Philadelphia Energy (Carlyle Group), Philadelphia, PA, 335,000 Bbl/day
11. WRB Refining, (WRB Refining) Wood River, IL, 333,000 Bbl/day
12. Chevron (Chevron USA Inc.), Pascagoula, MS, 330,000, Bbl/day

WORLD'S LARGEST REFINERIES

Table 3

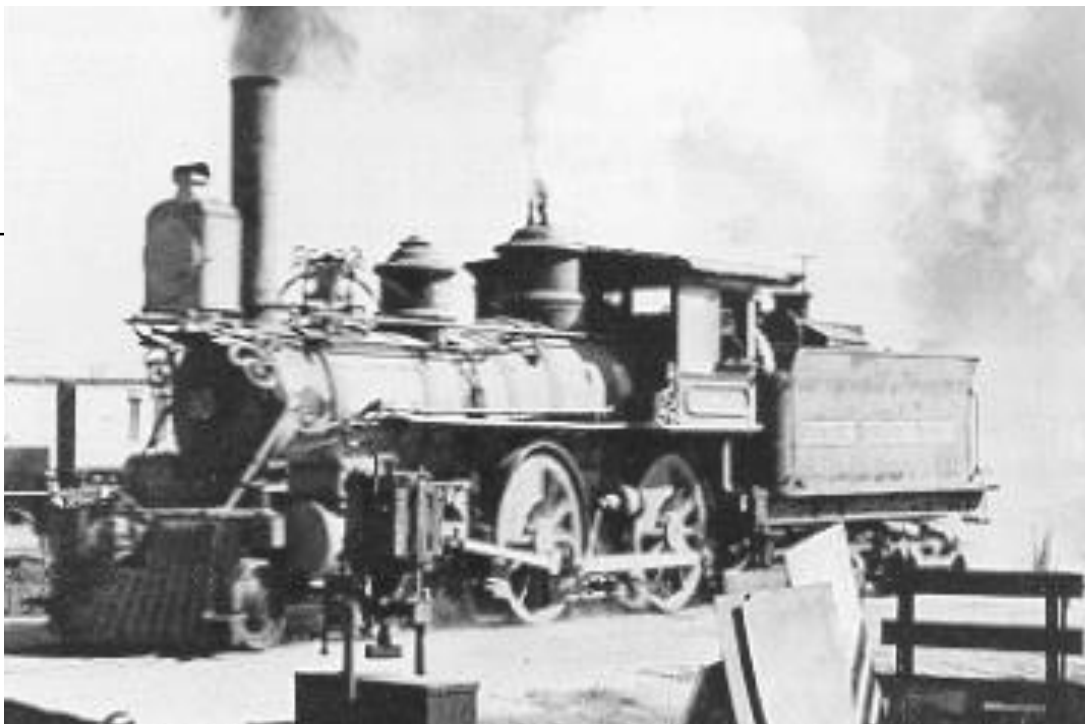
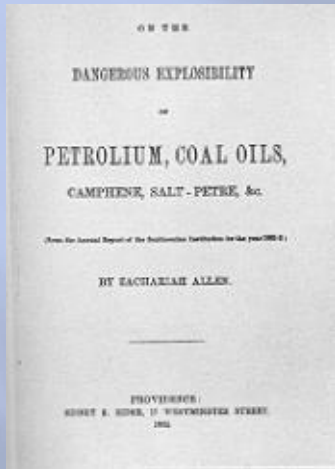
Company	Location	Crude capacity, b/cd
1 Paragana Refining Center	Cardon/Judibana, Falcon, Venezuela	940,000
2 SK Innovation	Ulsan, South Korea	840,000
3 GS Caltex Corp.	Yeosu, South Korea	760,000
4 Reliance Petroleum Ltd.	Jamnagar, India	660,000
5 ExxonMobil Refining & Supply Co.	Jurong/Pulau Ayer Chawan, Singapore	605,000
6 Reliance Industries Ltd.	Jamnagar, India	580,000
7 S-Oil Corp.	Onsan, South Korea	565,000
8 ExxonMobil Refining & Supply Co.	Baytown, Tex	560,500
9 Saudi Arabian Oil Co. (Saudi Aramco)	Ras Tanura, Saudi Arabia	550,000
10 Formosa Petrochemical Co.	Mailliao, Taiwan	540,000
11 ExxonMobil Refining & Supply Co.	Baton Rouge, La.	502,500
12 Hovensa LLC	St. Croix, Virgin Islands	500,000
13 Marathon Petroleum Co. LLC	Garyville, La.	490,000
14 Kuwait National Petroleum Co.	Mina Al-Ahmadi, Kuwait	466,000
15 Shell Eastern Petroleum (Pte.) Ltd.	Pulau Bukom, Singapore	462,000
16 BP PLC	Texas City, Tex.	451,250
17 Citgo Petroleum Corp.	Lake Charles, La.	440,000
18 Shell Netherland Raffinaderij BV	Pernis, Netherlands	404,000
19 Sinopec	Zhenhai, China	403,000
20 Saudi Arabian Oil Co. (Saudi Aramco)	Rabigh, Saudi Arabia	400,000
21 Saudi Aramco-Mobil	Yanbu, Saudi Arabia	400,000

ConocoPhillips Co., Ponca City: 198,400 barrels per day

- Holly Refining and Marketing Co., Tulsa (East): 70,300 barrels per day
- Holly Refining and Marketing Co., Tulsa (West): 85,000 barrels per day
- Valero Refining Co. Oklahoma, Ardmore: 85,000 barrels per day
- Wynnewood Refining Co., Wynnewood: 70,000 barrels per day



Refinery Class



Refinery Class



What Refineries Do

- They make useful products like:
 - gasoline
 - diesel fuel
 - jet fuel (JP-4, JP-5 and A-1)
 - heating oil
 - feed stock for petro-chemicals
- From Petroleum Crude



What Refineries Do

- They also make waste products:
 - air emissions
 - hazardous waste
 - waste water



Sources of Emissions

- **NO_x - Combustion Sources**
 - Fired Heaters (70%)
 - Fluid Catalytic Cracker (10-15%)
- **SO_x - Fuel Containing Sulfur**
- **CO - Incomplete Combustion**
- **VOC - Fugitive Emissions**
- **Miscellaneous Sources (50%)**



Summary of Regulations

- MACT
- NSPS
- Title V
- Fugitives
- Visible Emissions
- Fence line Monitoring
- Review of Refinery NSPS/NESHAP/MACT Standards Handout



High Priority Sources

- Fired Heaters
- Flares
- Catalytic Cracking
- Sulfur Recovery
- Fugitive Emissions
- Storage Tanks
- Wastewater Treatment
- Cooling Towers
- Vacuum Systems



Crude Oil Terms

- Heavy-Light Crude
- Sweet-Sour Crude
- API Gravity



Petroleum Chemistry

- Nomenclature
- Physical Properties
- Structure



Nomenclature

- C1 = Methane (C_1H_4)
- C2 = Ethane (C_2H_6)
- C3 = Propane (C_3H_8)
- C4 = Butane (C_4H_{10})
- C5 = Pentane (C_5H_{12})
- C6 = Hexane (C_6H_{12})
- C8 = Octane (C_8H_{18})- Octane Rating
- C16 = Cetane ($C_{16}H_{34}$)- Cetane Rating

Physical Properties

- Boiling point
- Structure
- Reactivity
 - Exothermic
 - Endothermic



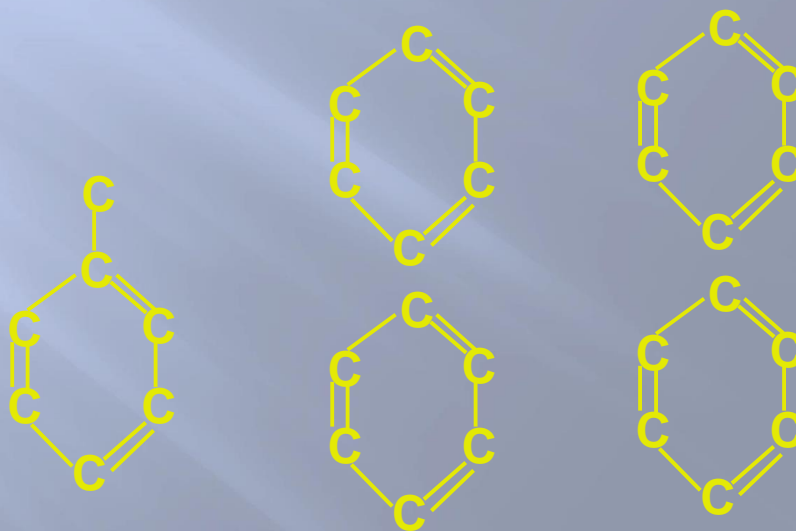
Physical Properties

NAME	FORMULA	BOILING POINT
Methane	CH ₄	-162
Ethane	C ₂ H ₆	-88.5
Propane	C ₃ H ₈	-42
n-Butane	C ₄ H ₁₀	0

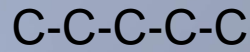
Structure

- Paraffin (straight chain - saturated)
 - Normal c-c-c-c
 - Branched (iso)
- Napthenes (ring or cyclo)
- Olefins (double bond)
 - unsaturated C= C-C-C
- Aromatics (cyclo-resonating bonds)

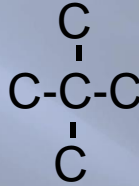
Aromatics



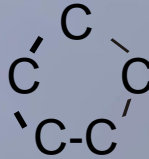
**PENTANES
(Paraffin)**



62
Octane

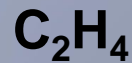
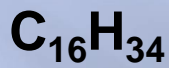


120
Octane



80
Octane

Cracking Expansion



7.2 lbs
1 gallon



7.2 lbs
1.3 gallons

Crude Oil Assay

AMS CRUDE BLEND REPORT FOR WEEK ENDING NOV 20, 1987

CRUDE PROPERTIES				
Assay Gravity		27.1		
Sulfur, wt%		1.16		
Nitrogen, ppm		2009		
Concarbon, wt %		4.79		
Nickel, ppm		12		
Vanadium, ppm		26		
CRUDE BLEND DATA		Vol%		
Defined Components Analysis				
C2		0.04		
C3		0.33		
iC4		0.44		
nC4		1.53		
iC5		0.81		
nC5		1.14		
C6+		95.71		
Total		100.00		
TEP Distillation	API Grav	Sulfur Wt%	Diff Vol %	Cum Vol %
C4-	124.0	0.00	2.4	2.4
150 F	74.7	0.00	3.5	5.9
200 F	59.6	0.00	2.4	8.2
250 F	54.3	0.00	3.1	11.3
300 F	50.0	0.00	3.6	14.9
350 F	47.1	0.00	3.7	18.5
400 F	43.5	0.01	3.9	22.5
450 F	36.8	0.10	4.9	27.3
500 F	34.0	0.30	5.2	32.5
550 F	31.7	0.47	4.7	37.2
600 F	30.6	0.64	5.7	42.8
650 F	27.0	0.85	5.3	48.3
700 F	25.4	0.99	4.1	52.4
750 F	23.8	1.09	4.4	56.8
800 F	22.5	1.21	4.1	60.9
850 F	20.9	1.34	4.3	65.1
900 F	19.3	1.49	4.0	69.1
950 F	17.6	1.64	4.2	73.3
1000 F	16.0	1.80	4.0	77.3
1050 F	13.6	1.89	3.9	81.2
1100 F	11.4	1.97	3.6	84.8
1100+ F	4.9	2.42	15.2	100.0

Quick Review 1

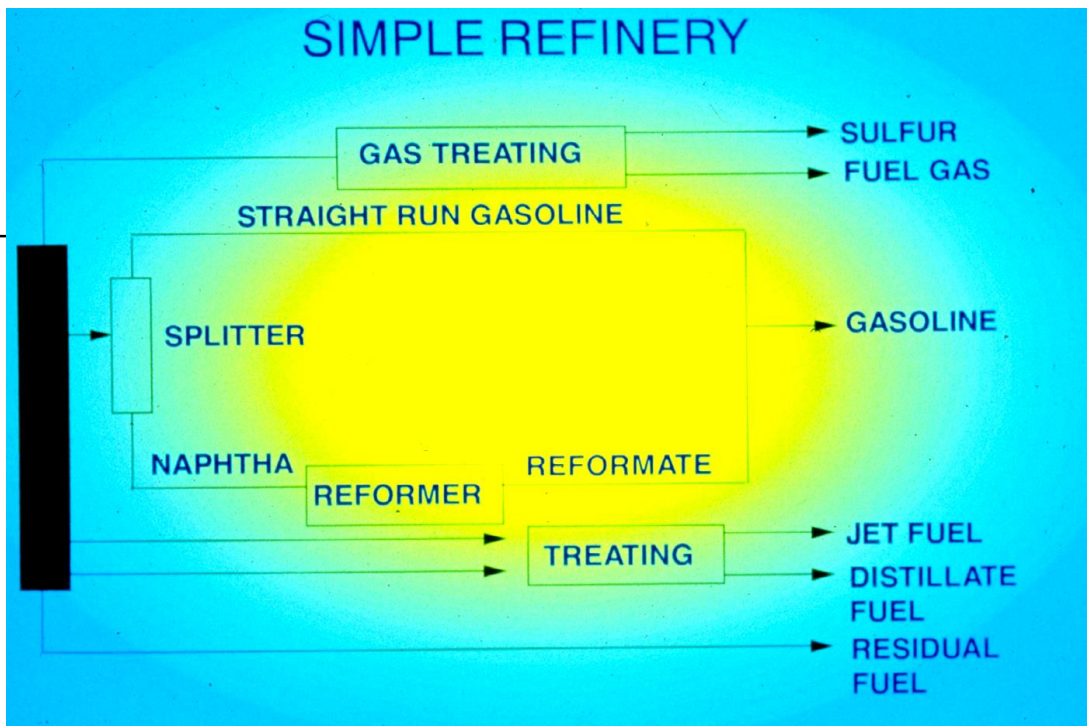
- Primary Sources of emissions
 - Combustion
 - Fugitive
 - Process particulates
- Regulations & Requirements
 - NSPS, Part 61 & 63 NESHAPS, MACT, general SIP
 - Plus NSR/PSD permits, Title V, NSR consent decree
- Crude Petroleum classifications
 - Sweet/sour
 - Light/heavy
- Chemistry
 - Nomenclature
 - Physical properties
 - Structure
 - Octane
 - Expansion

Process Units by Refinery Type

Simple	<ul style="list-style-type: none">-Crude Distillation-Hydrotreating of Middle Distillation-Catalytic Reforming of Naptha
Complex-Simple Plus	<ul style="list-style-type: none">-Vacuum Distillation-Catalytic Cracking-Alkylation Plant-Gas Processing
Very Complex	<ul style="list-style-type: none">-Olefin Unit
-Complex Plus	<ul style="list-style-type: none">-Residue Reduction (Coker)



Simple Refinery



Complex Refinery



Very Complex Refinery



Complexity and Yields

<u>Fuel Type</u>	<u>% Yield</u>		
	Simple	Complex	Very Complex
Gasoline	30	50	65
Jet Fuel	10	19	20
Distillate Fuel	20	17	25
Residual Fuel	35	20	0
Total	95	106	110
Gain	-5	6	10

EQUIPMENT COMBUSTION

Equipment Used in the Refining Process

- Fired Heaters
- Heat Exchangers
- Flares
- Cooling Towers
- Vacuum Jets
- Storage Tanks
- Pumps, Valves and Compressors

Fired Heaters

PURPOSE: To transfer heat from the combustion of fuels to water, oils, gases, or other fluids



Two Types of Fired Heaters

- Boilers - Designed for steam generation
- Process Heaters/Furnaces - Designed to heat liquid, oils and gases other than water



Process Heaters

Cabin Type



Upright Type



Multi-Pass Process Heater



Emissions From Boilers/Heaters

**Fuel
+
Air
(N₂, O₂)**



- H₂O
- CO₂
- CO
- NO_x
- HC
- SO_x
- PM
- CHO

Types of Fired Heaters

- Natural Draft Heater
- Forced Draft Heater
- Induced Draft Heater
- Balanced Draft Heater

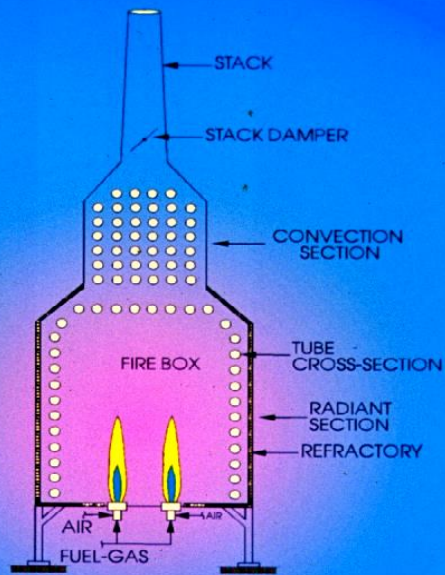
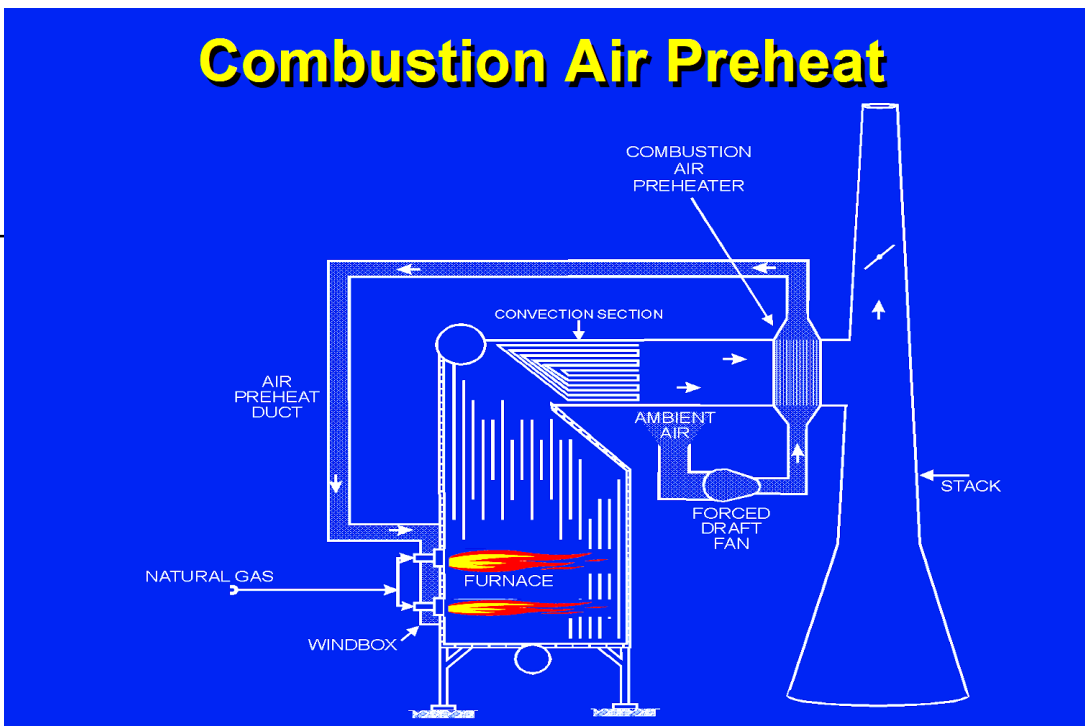
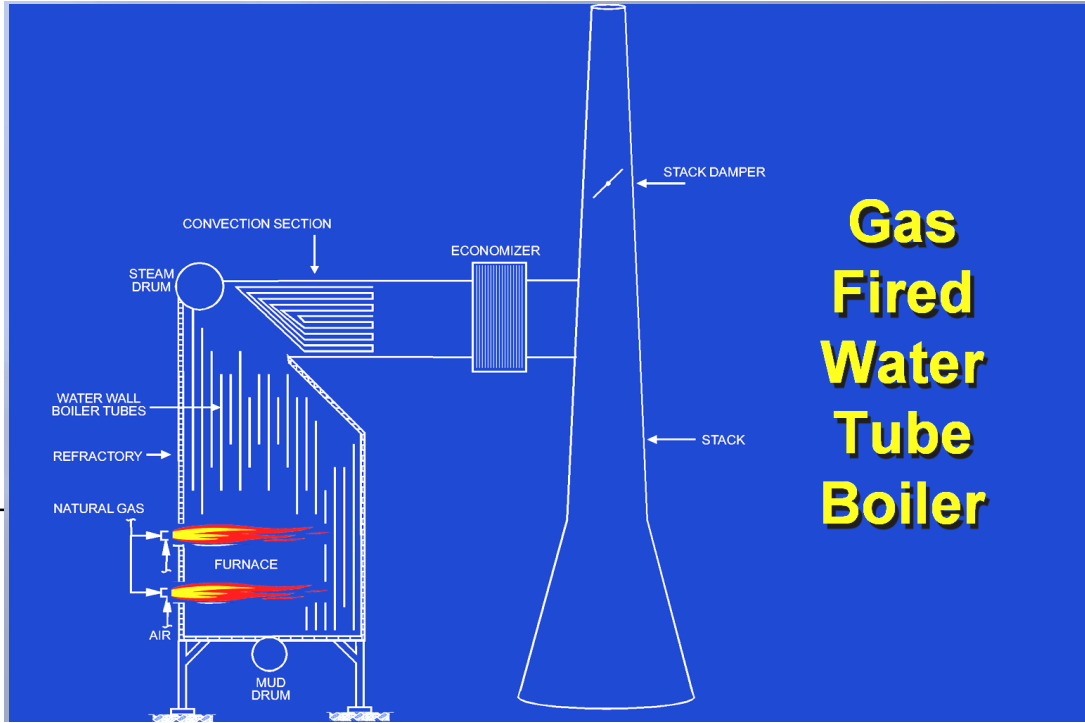


Figure 201.1
Conventional Gas-Fired Heater





**Stack
Damper
on
Natural
Draft
Heater**

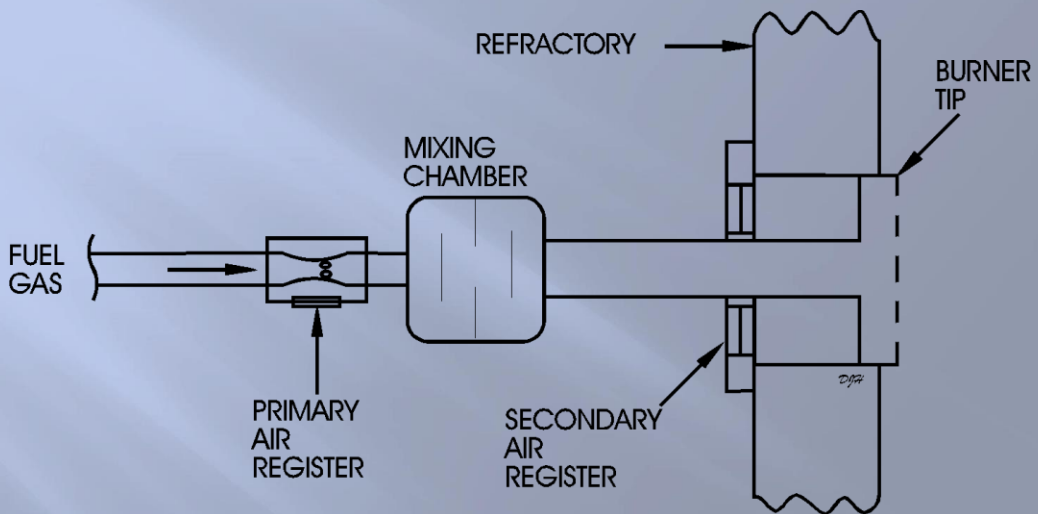
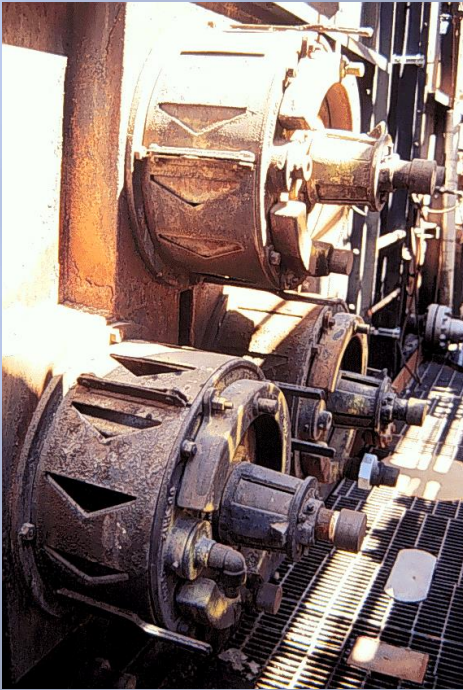
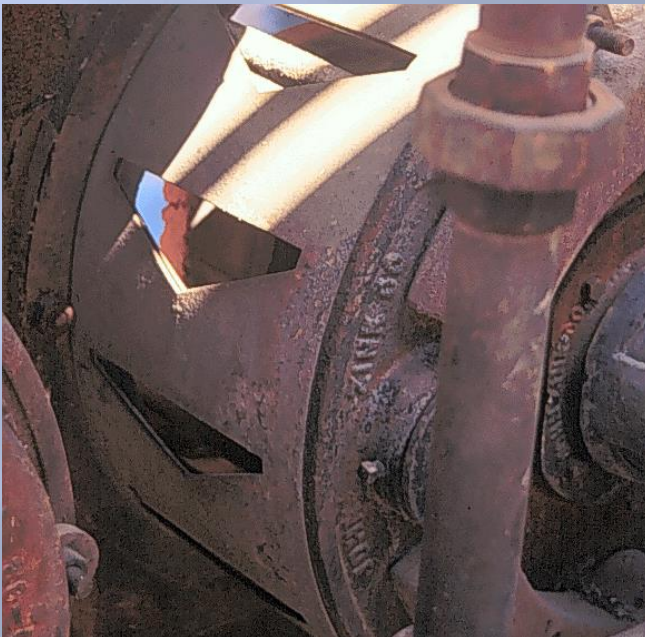


Figure 201.2
Gas Pre-mix Burner



**Burner
Assemblies**



**Close
Up of
Air
Registers
on
Burner**

Flames inside of a Firebox



Forced and Induced Draft Fans on a Heater



Up-Fired Burners with Pre-Heated Air

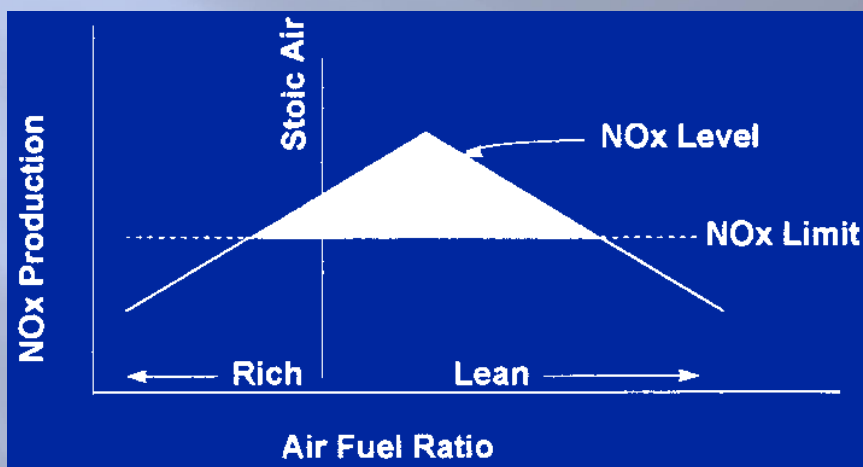


Up-Fired Burners with Pre-Heated Air

Pollutant Control Requirements

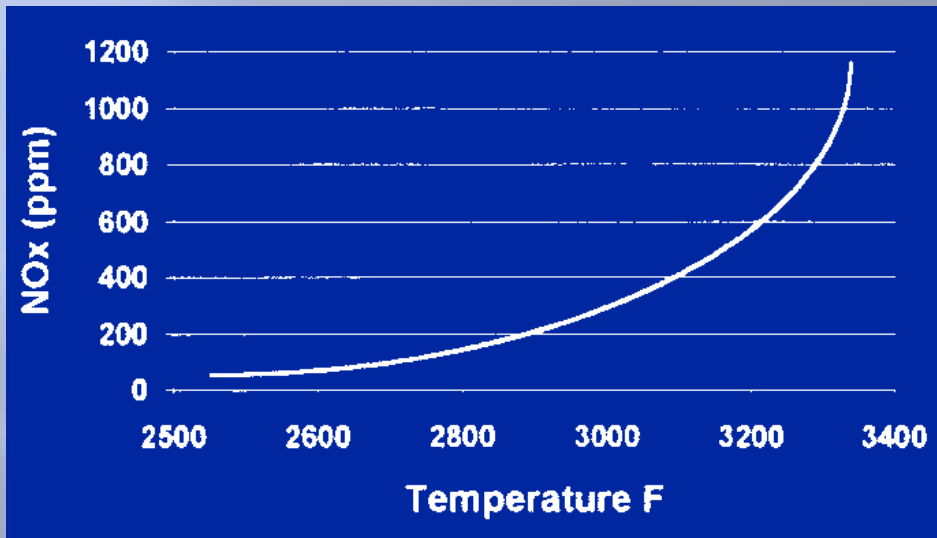
- NOx
 - Flue Gas Recirculation (FGR)
 - Low NOx Burners
 - Selective Catalytic Reduction (SCR)
 - Selective Non-Catalytic Reduction
- SOX
 - Limiting the amount of sulfur in the fuel gas
 - Post Combustion SO₂ Scrubbers

NOx Production vs. Air/Fuel Ratio



Graphic Courtesy of Coen

Thermal NO_x vs. Temperature



Graphic Courtesy of Coen

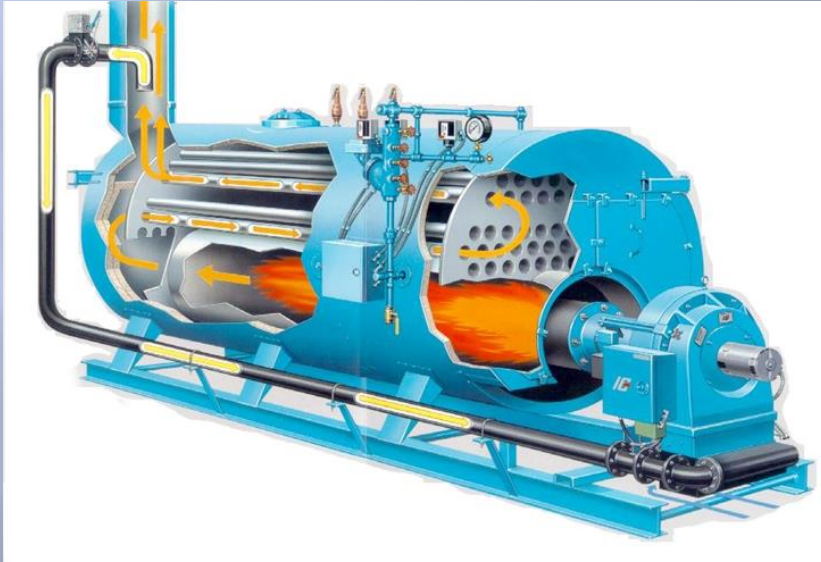
NO_x Control Methods

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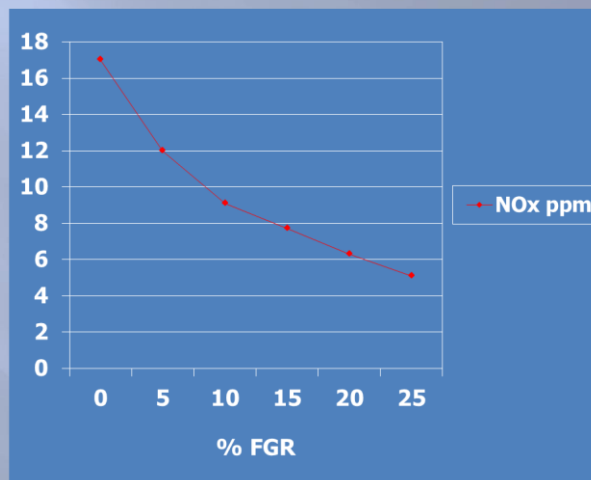
- Flue Gas Recirculation (FGR)
- Low NO_x Burners
- Selective Catalytic Reduction (SCR)
- Selective Non-Catalytic Reduction



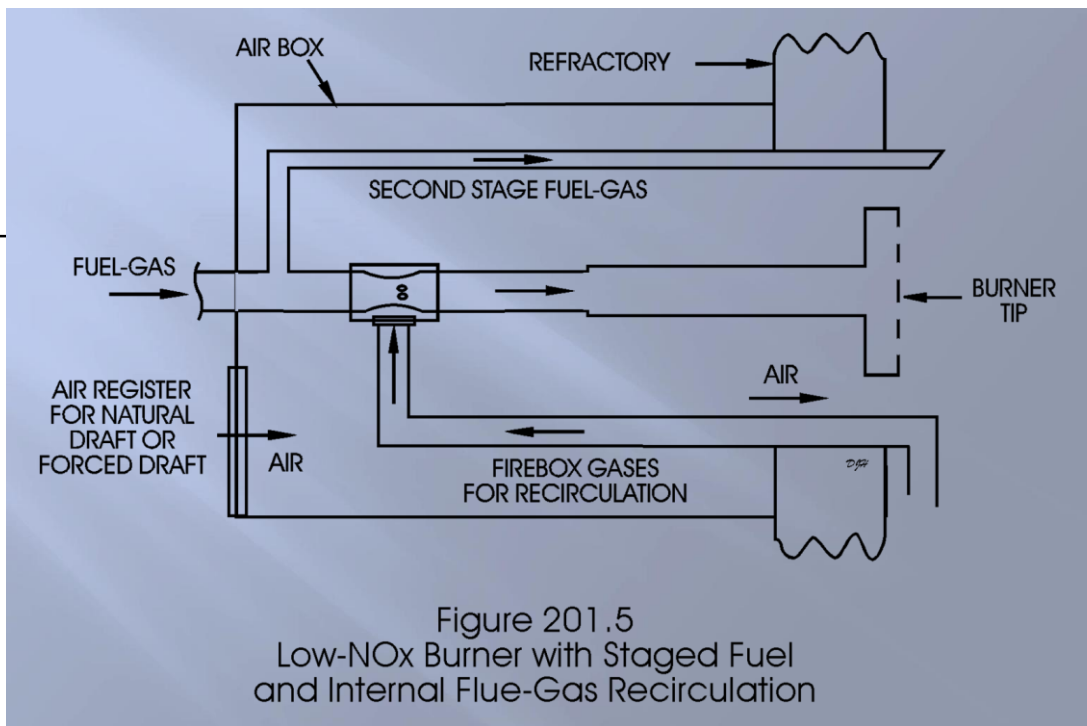
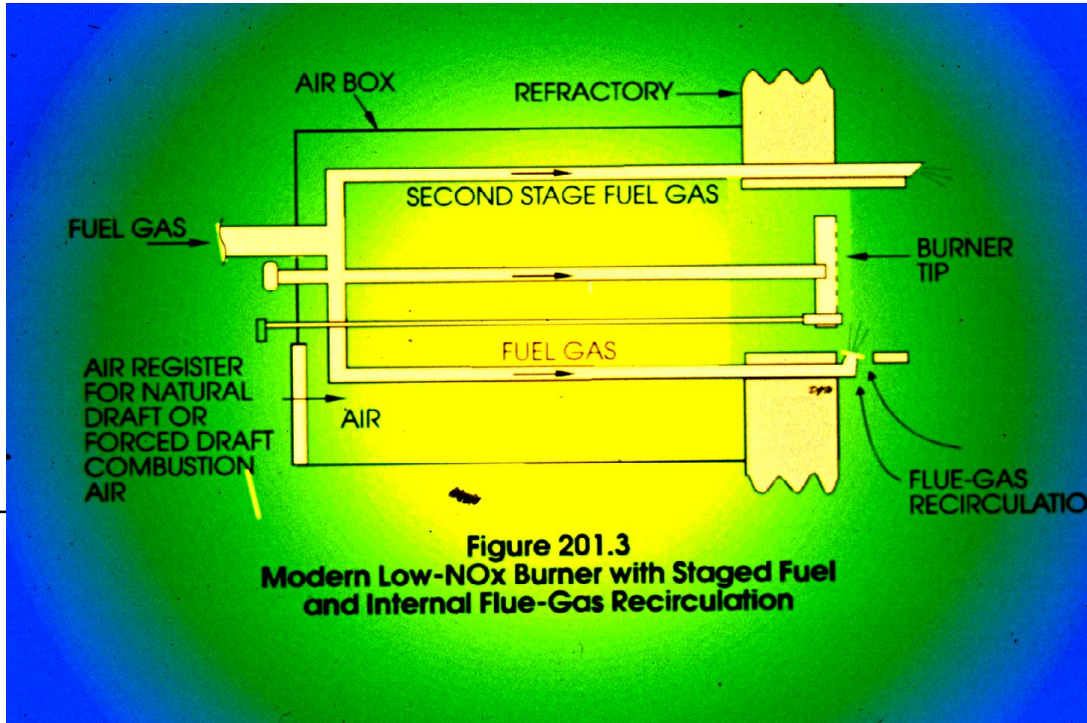
Flue Gas Recirculation (FGR)



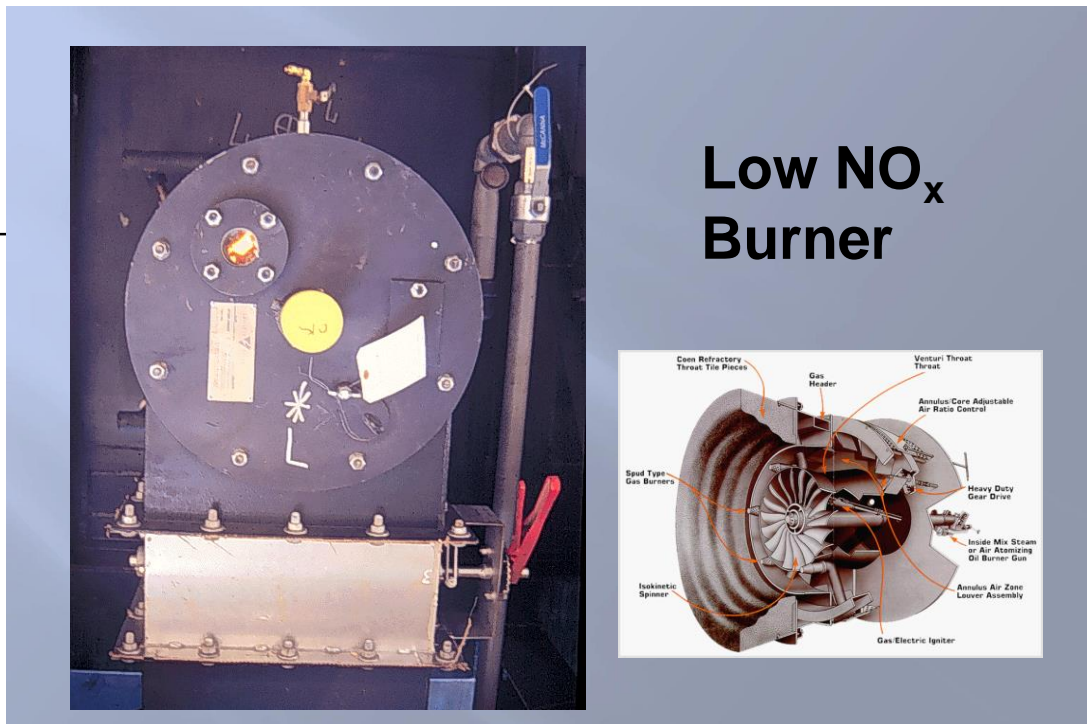
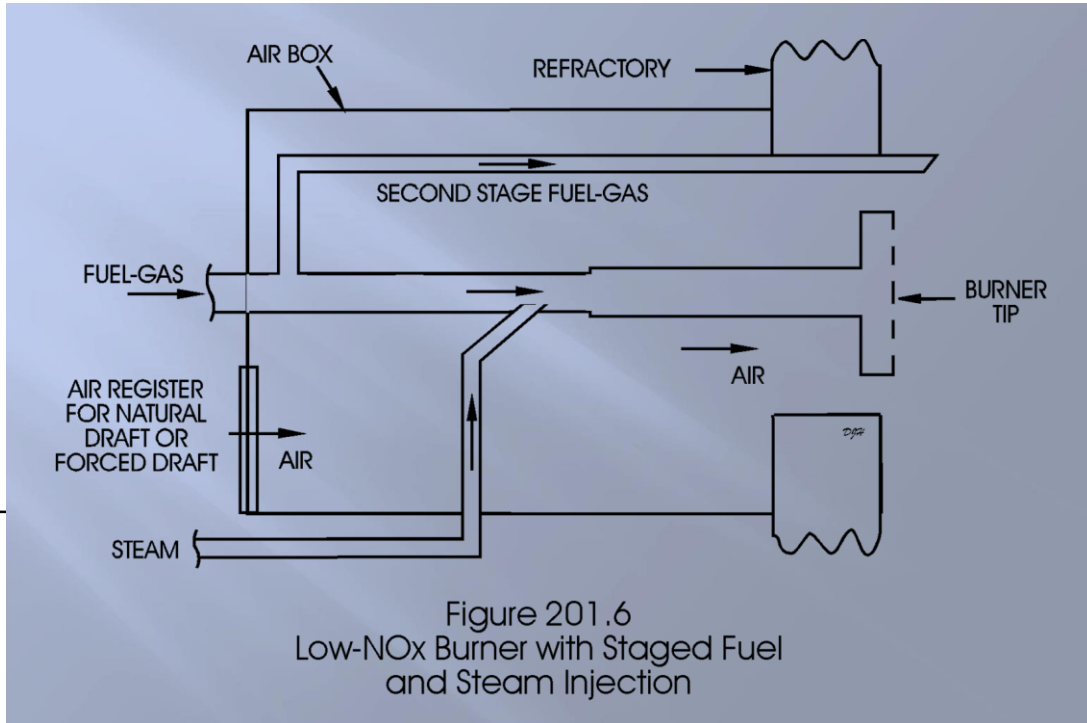
FGR Impact

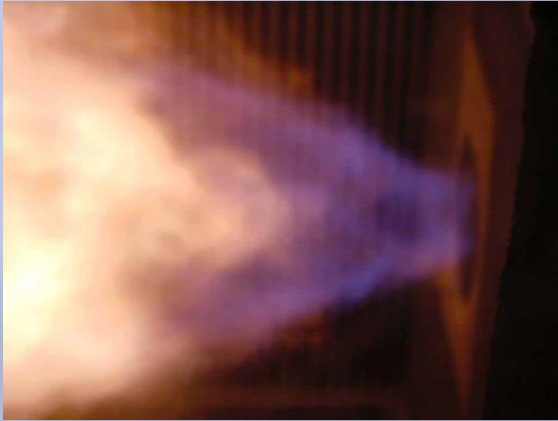


Refinery Class



Refinery Class





**Low NO_x
Burner
Flames**



Conventional Burner



Conventional Burner & FGR



Low NOx Burner

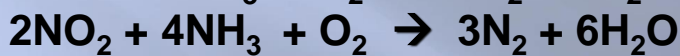
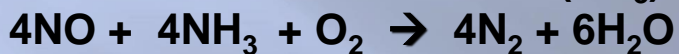


Low NOx Burner & FGR



Selective Catalytic Reduction (SCR)

NO_x control thru ammonia (NH₃) injection



65-90% control

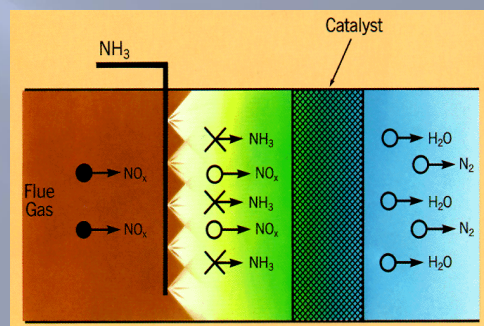
Problems

Expensive

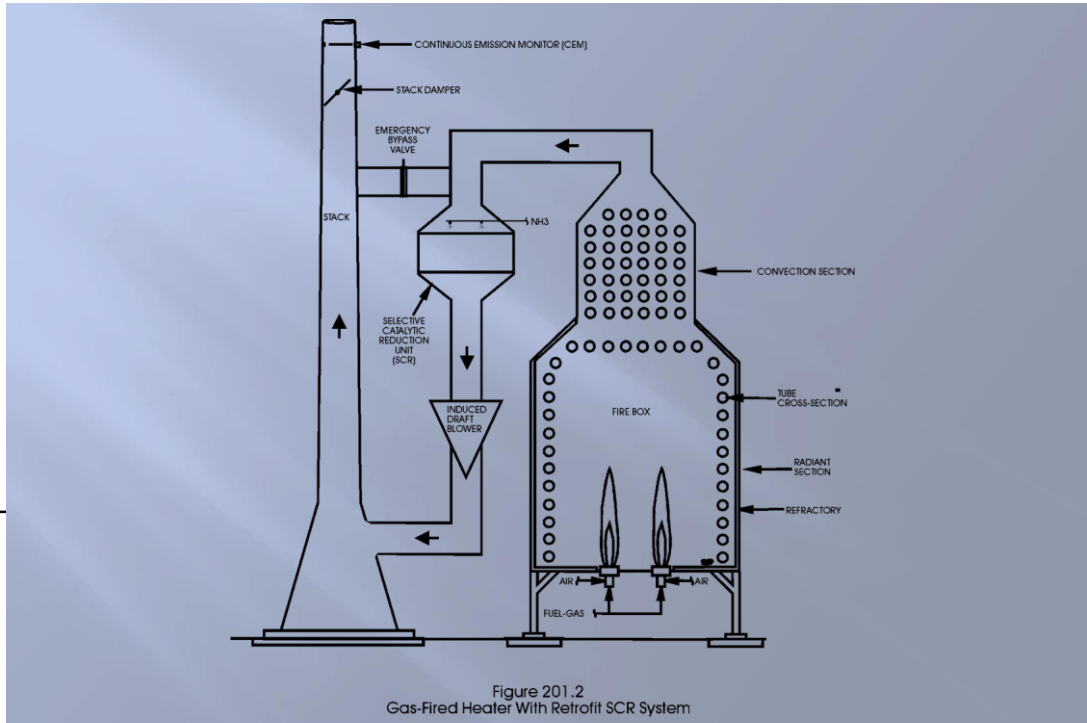
High maintenance

Ammonia "slip"

Catalyst replacement
& disposal



Refinery Class



Selective Catalytic NO_x Reduction (SCR)





Ammonia Injection System for SCR

Selective Non-Catalytic Reduction

NO_x control through ammonia or urea injection

No catalyst necessary

Temperature range 1400 °F – 2000 °F

Injected upstream of convection section

30% - 50% control under normal conditions

Problems:

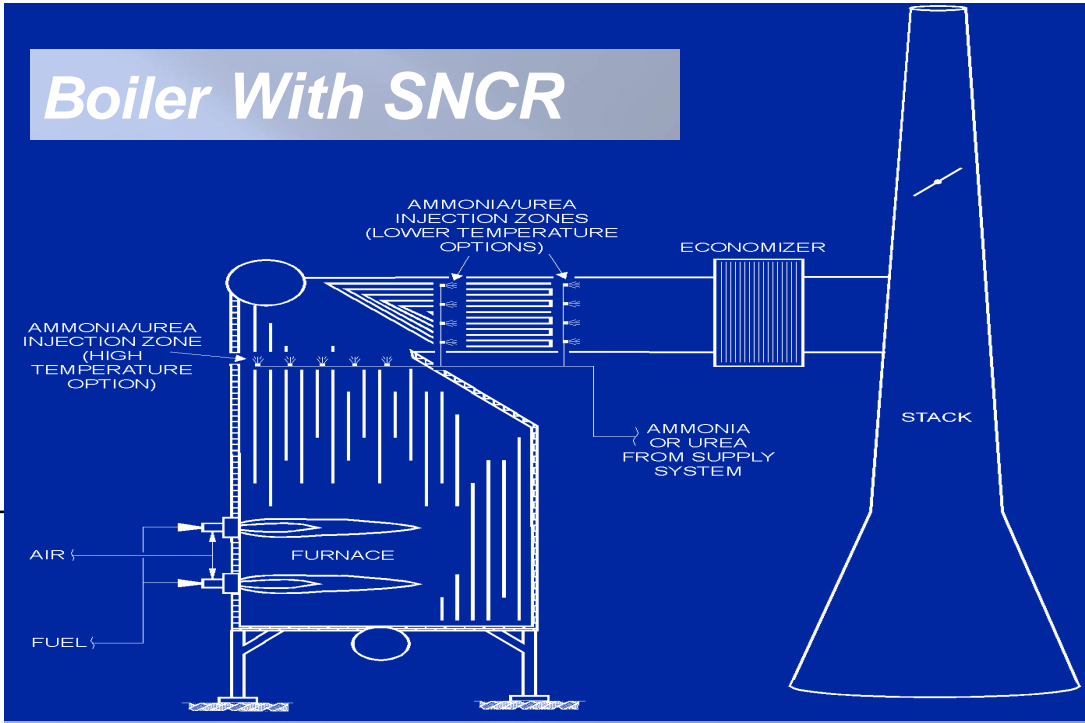
Changing flue temperatures with changing load

Formation of ammonium salts

Ammonia slip



Boiler With SNCR



Ammonia Storage



Inspection of SNCR

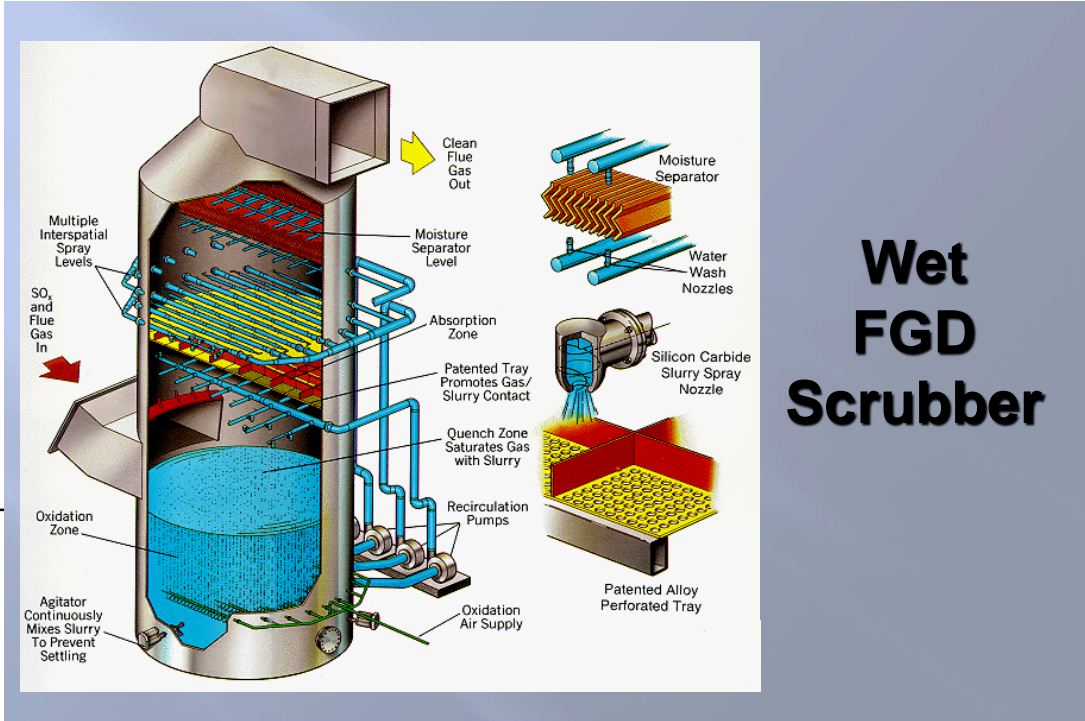
- Ammonia injection rate
- Operating temp 1400-1900 deg F
- May be required to test stack for ammonia slip.

- Contrasted to SCR that will often have CEMs for SCR temp should be 550-750 deg F



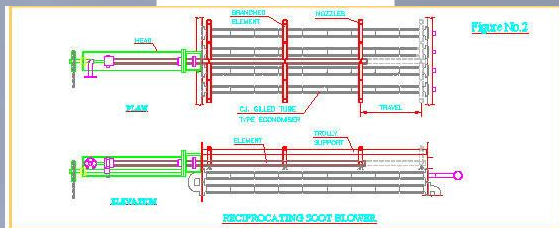
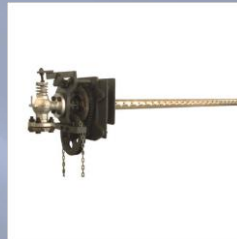
Waste Gas Burning





Soot Blowing

Blowing Dust From Boiler Tubes Using Steam Or Air



Fired Heaters

- **INSPECTION POINTS:**
 - Fuel (BTUs, sulfur)
 - Control Equipment check
 - Permit conditions
 - Visible Emissions
 - Flame observation



Regulations

- **NSPS**
- **Boiler MACT**
- **Visible Emissions**
- **Local Regulations**
- **Permit Conditions**



Heat Exchangers

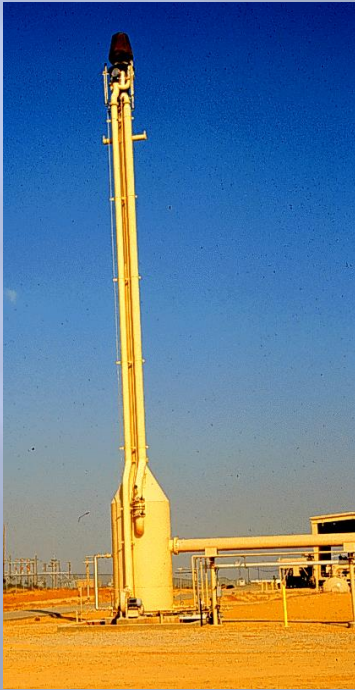
Purpose: An energy conservation device used to transfer heat from a relatively hot fluid stream to a relatively cool fluid stream.



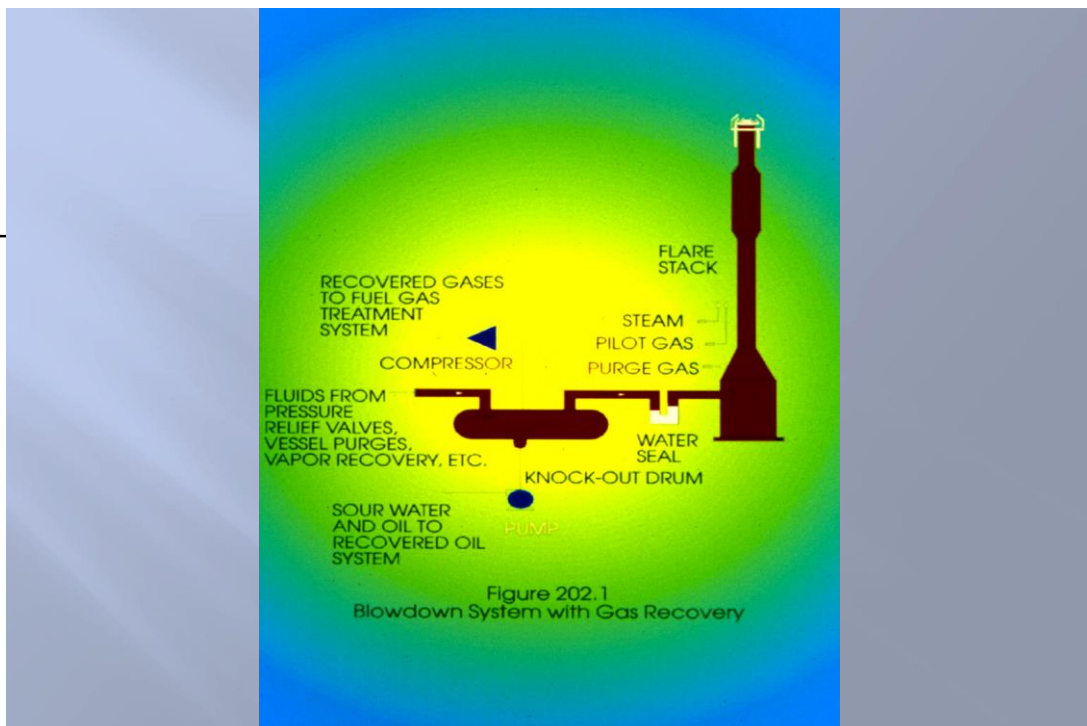
Flares

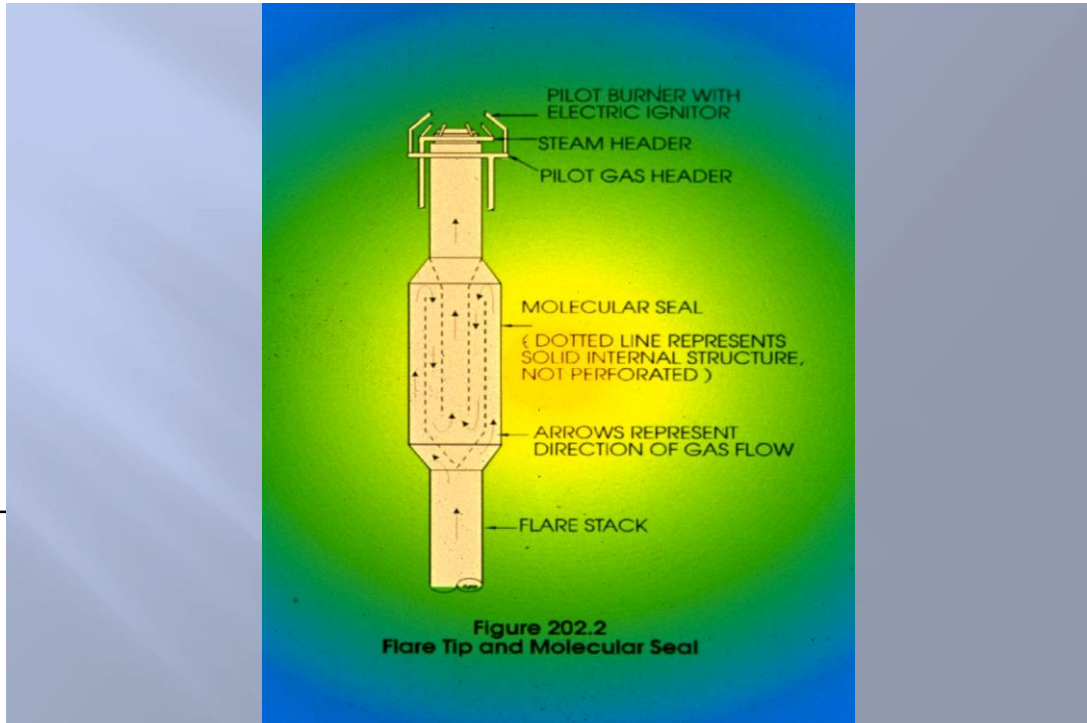
- PURPOSE: Emergency relief system for safe depressurizing of refinery process operations.
- Vented gases are burned at the tip of the flare.





Flare





Flare With Smokeless Flame





**Smokeless
Flare
Tip**

Relief System - Knockout Drum





Base of Flare

**Steam System for Flare
Smokeless Operation**

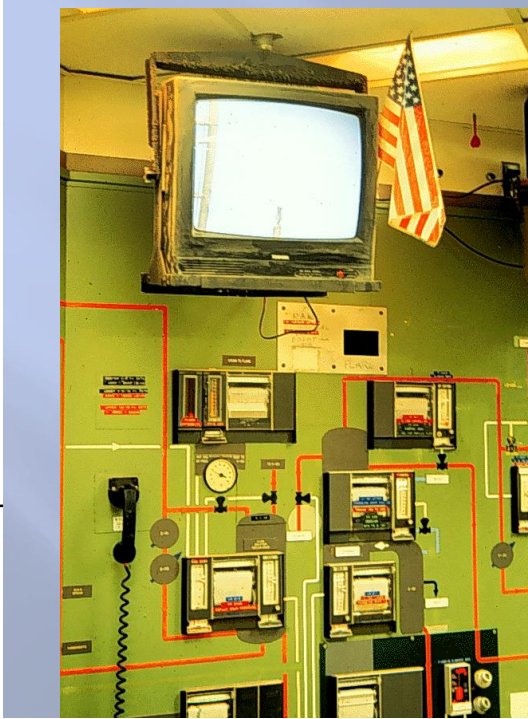


Water Seal Level for Flare



Continuous Overflow from the Water Seal





Video Monitor on Flare

Flares

- REGULATIONS:
 - NPSP
 - 40 CFR 60.18
 - Subpart QQQ Section 60.692-5 (c)
 - Subpart Kb, Section 60.113(b)
 - Subpart GGG, Section 60.592 (a)
 - Nuisance and odor issues
 - More tomorrow

Flares Continued

- REGULATIONS:
- Visible Emission Evaluation (VEE)
- Odors
- SO_x



Flares

- INSPECTION POINTS:
 - Visible Emission Evaluation (VEE)
 - Pilot Light
 - Odors
 - Gas Compressor if applicable
 - Water Seal
 - Flow Rates
 - Odors/Ground level SO₂



EQUIPMENT (FUGITIVE VOC)

Coolers

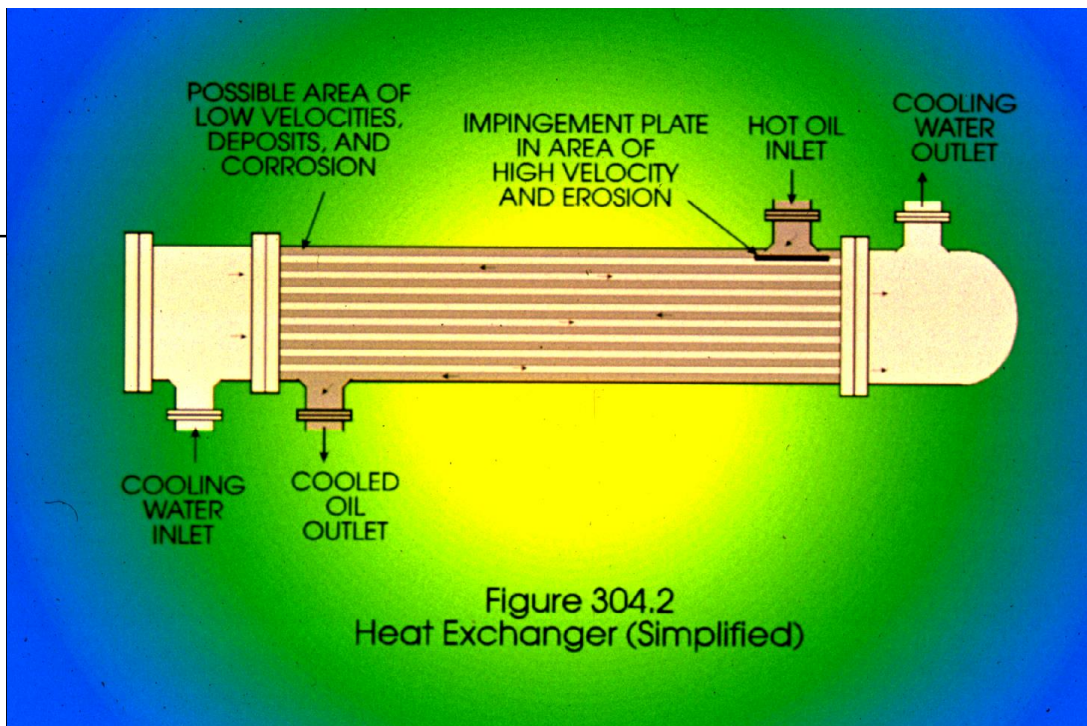
Purpose: Use air to cool or condense process streams



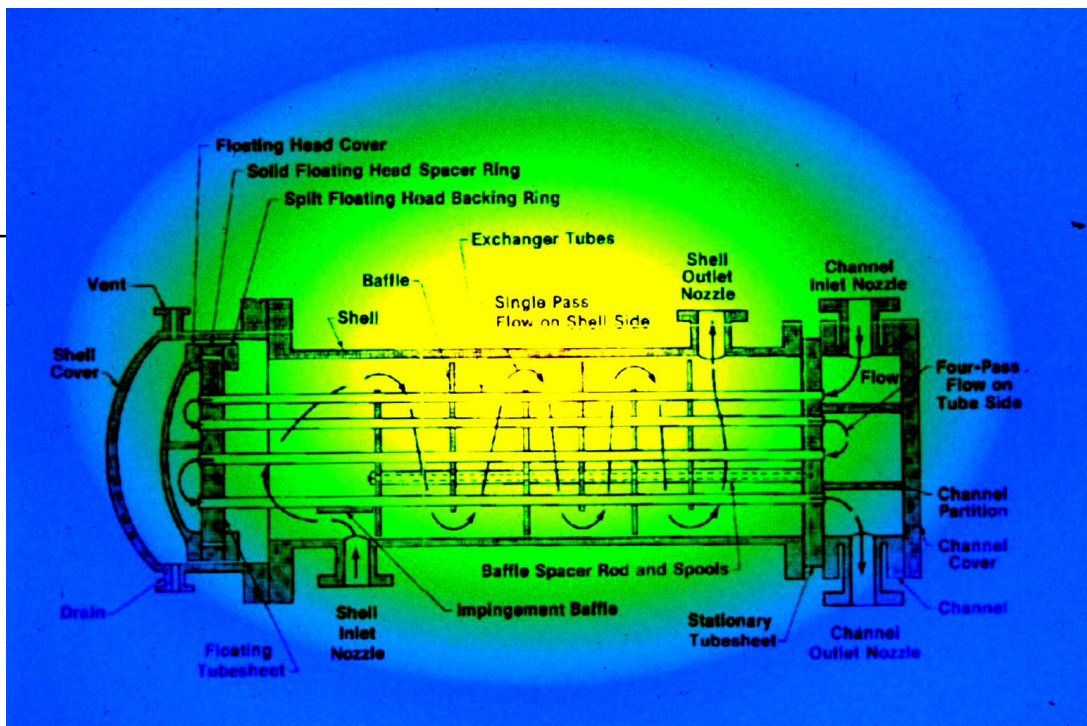
Heat Exchangers Used in Conjunction with Air Coolers



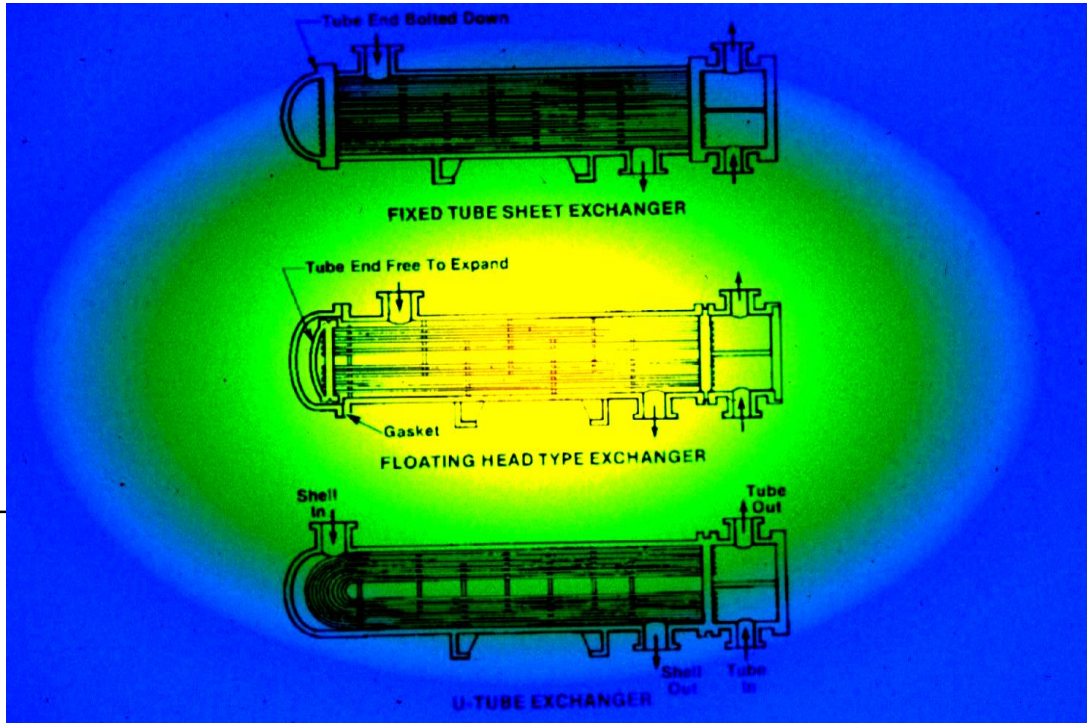
Heat Exchangers



Heat Exchanger Bundle



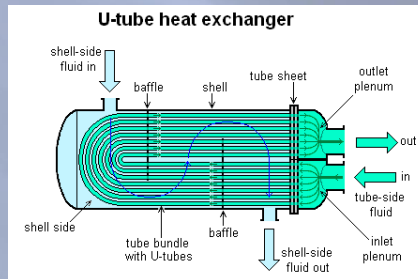
Refinery Class



Air Cooling Fans

Why Do They Leak

- Corrosion (pitting)
- Erosion (thinning of tubes)



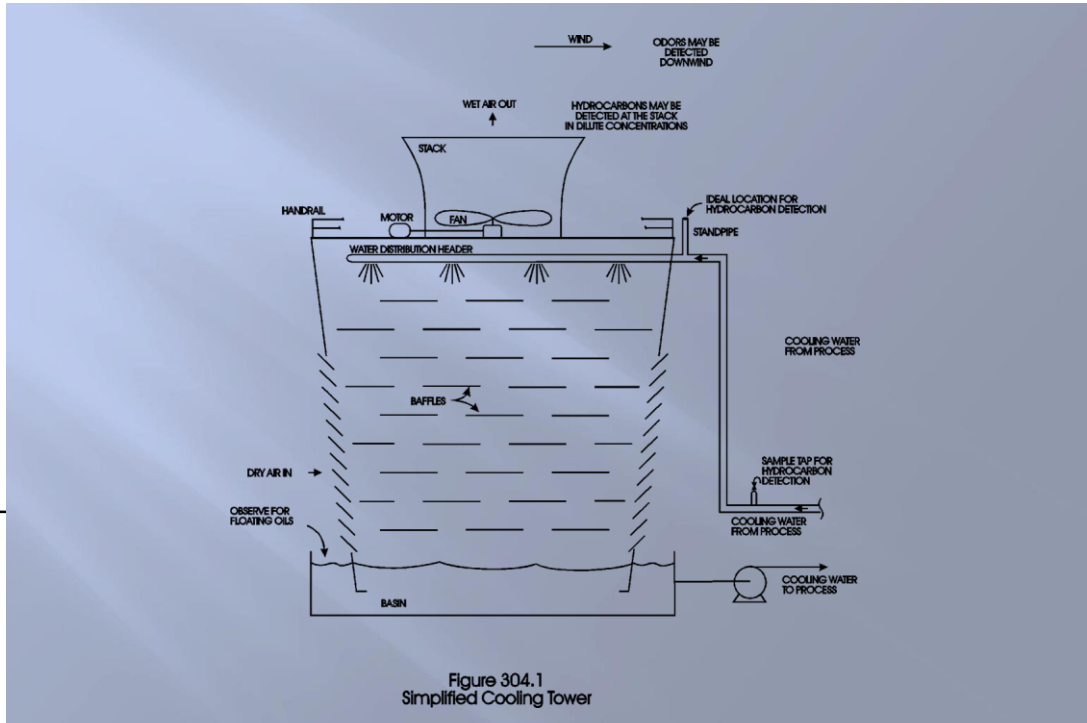
"U-tube heat exchanger". Licensed under CC BY-SA 3.0 via Commons - https://commons.wikimedia.org/wiki/File:U-tube_heat_exchanger.PNG#/media/File:U-tube_heat_exchanger.PNG

Cooling Towers

- PURPOSE: Used to cool water which had been warmed when circulated through process cooling equipment (exchangers)
- REACTION: Cools through evaporation of water into the air



Refinery Class



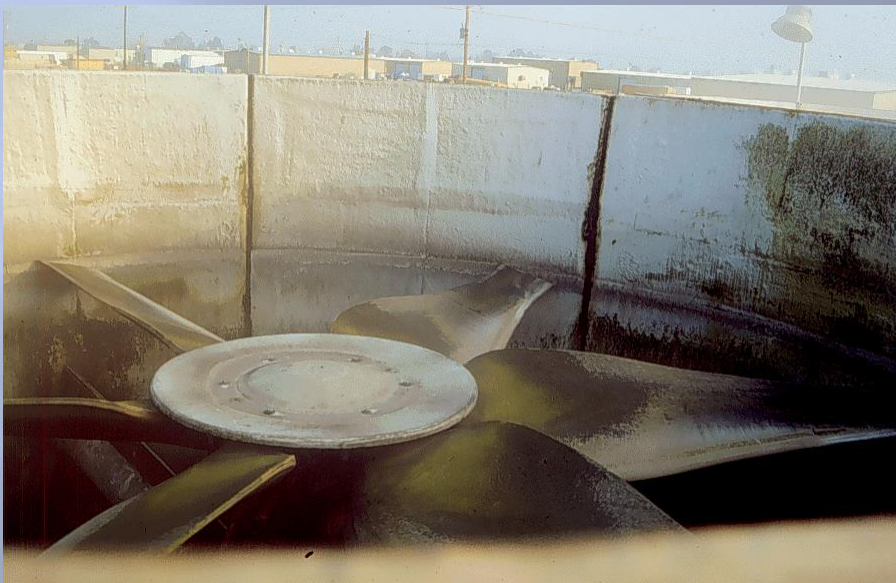
Cooling Tower

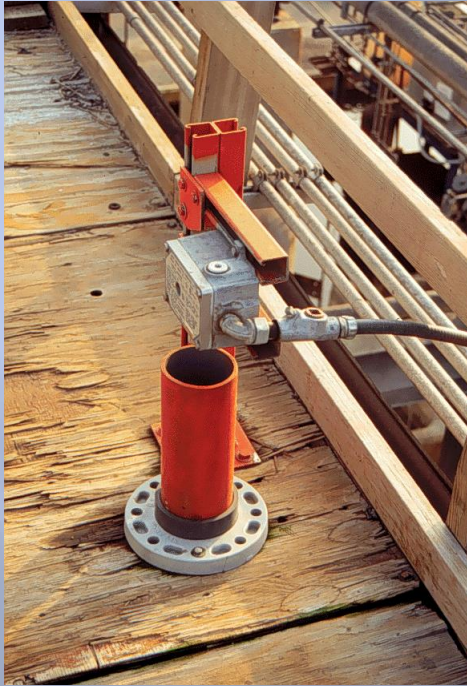


Risers Entering the Cooling Tower



Fan on Cooling Tower





Hydrocarbon Detector on a Riser Vent

Cooling Towers

- REGULATIONS:
 - Fugitive Emissions
 - No hexavalent chrome additives (corrosion inhibitor)
 - Odors



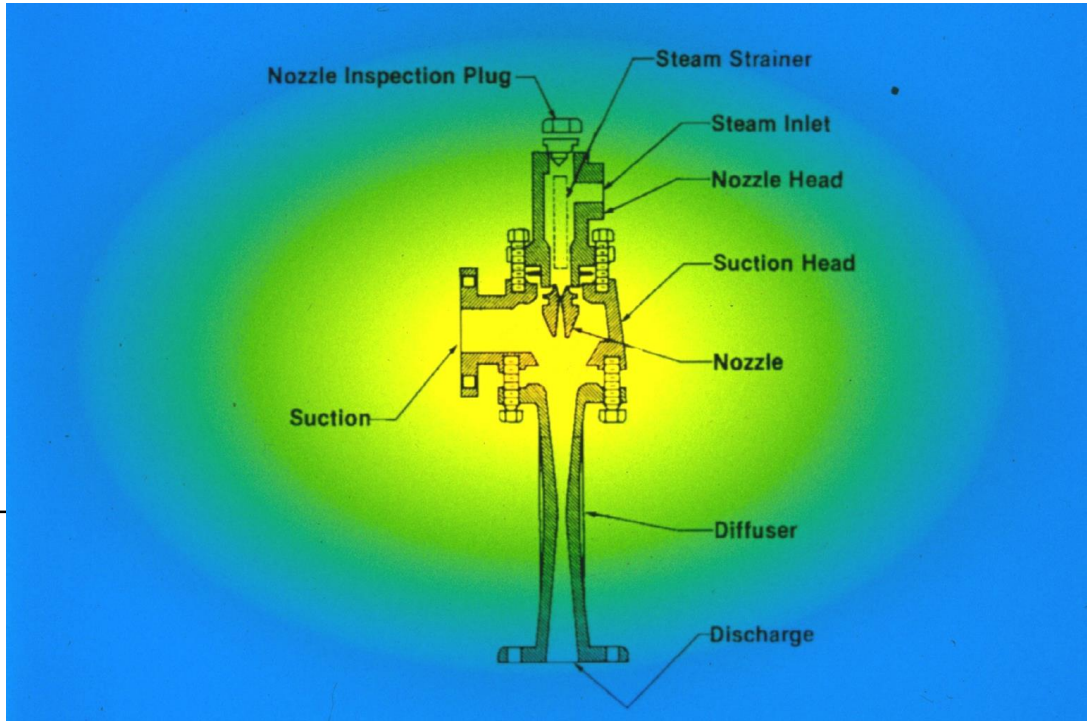
Cooling Towers

- Inspection Points:
 - Fugitive VOC's
 - Hexavalent chrome
 - Permit conditions
 - Odors

Steam Jet Ejectors

- **PURPOSE:** To remove gases from the vacuum flasher to create the vacuum
- **MECHANISM:** Uses a nozzle to increase the velocity and momentum of the steam. The high velocity and momentum draw a vacuum in the area beside the nozzle.

Refinery Class



Steam Ejectors on a Vacuum Distillation Unit - First Stage



Steam Ejectors on a Vacuum Distillation Unit - Second Stage



Steam Ejector System on a Vacuum Distillation Unit

Steam Jet Ejectors

- Inspection Points:
 - Where do the noncondensables go?
 - Permit conditions
 - Covered condensate accumulator vessel (hot well)

Storage Tanks - Types

- Conservation tanks
- Pressure tanks
- Fixed roof tanks
- Internal floating roof tanks
- External floating roof tanks



Conservation Tanks

- Tanks designed to hold vapors
- Have internal flexible diaphragms, lifter roofs, or blankets
- Often found in vapor recovery systems

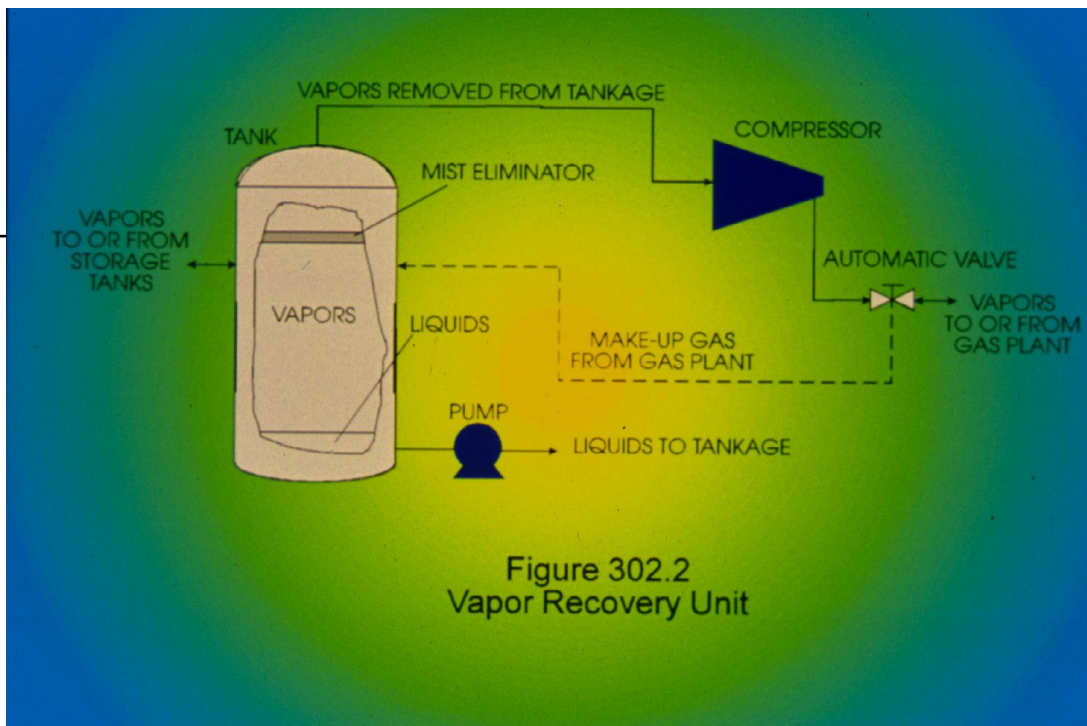
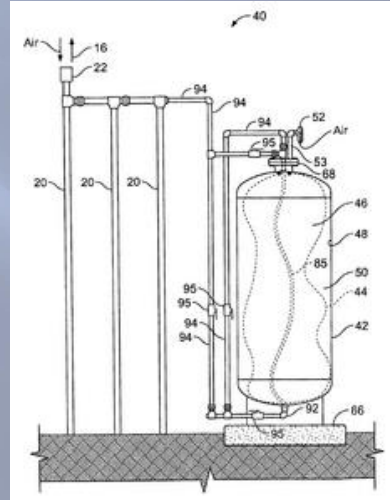


Figure 302.2
Vapor Recovery Unit

Pressure Tanks

- A special type of fixed roof tank that are designed to operate above atmospheric pressure
- Commonly used to store liquefied petroleum gases (LPG)



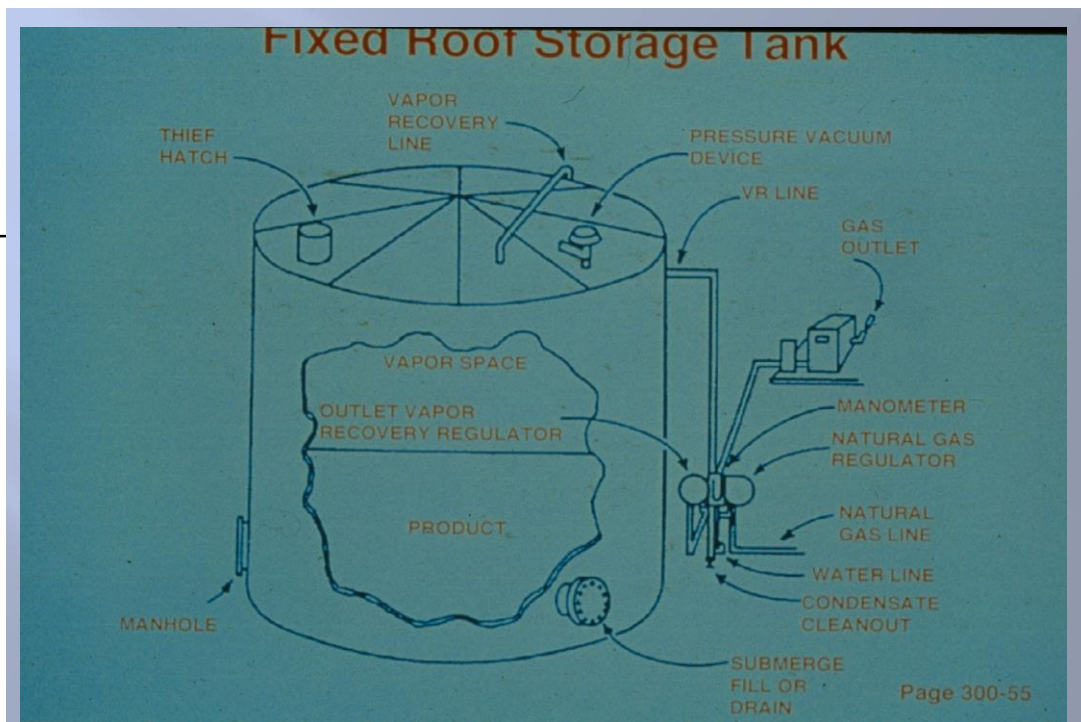
Fixed Roof Tanks

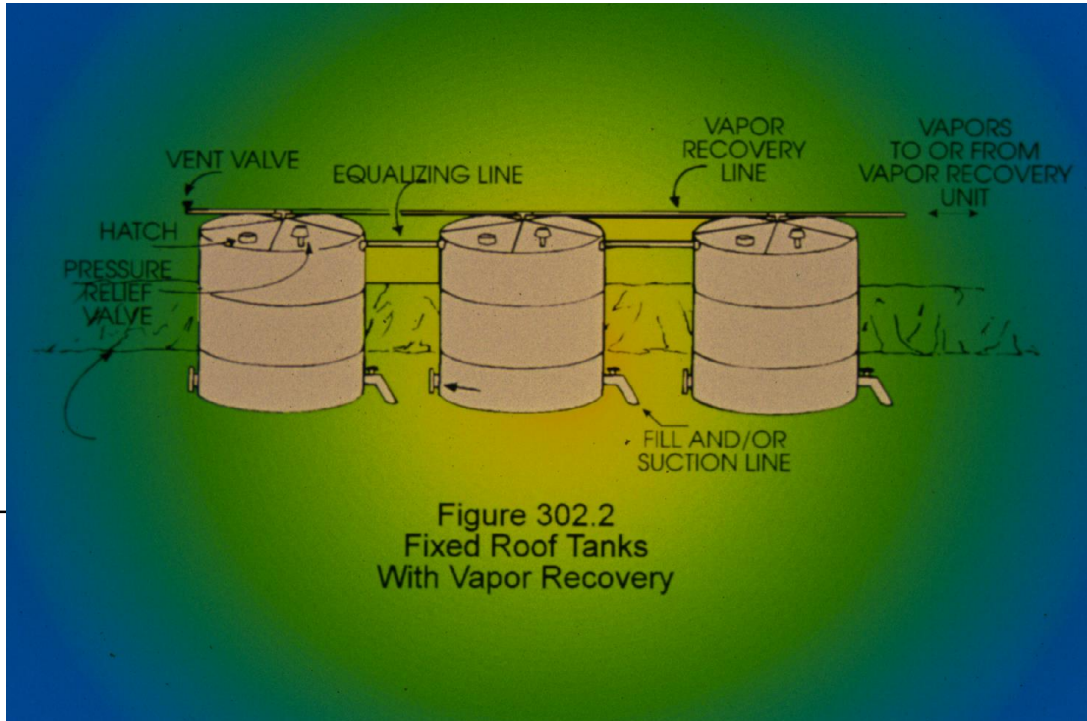
- Cylindrically shaped vessels made of steel that are welded or riveted together and covered by a stationary roof
- The roof is generally conical in shape thus these tanks are also known as cone roof tanks



Fixed Roof Tanks

- VOC emissions (breathing losses and diurnal losses) are controlled by:
 - Vapor Recovery
 - Gas Blanketing (Test Warning)

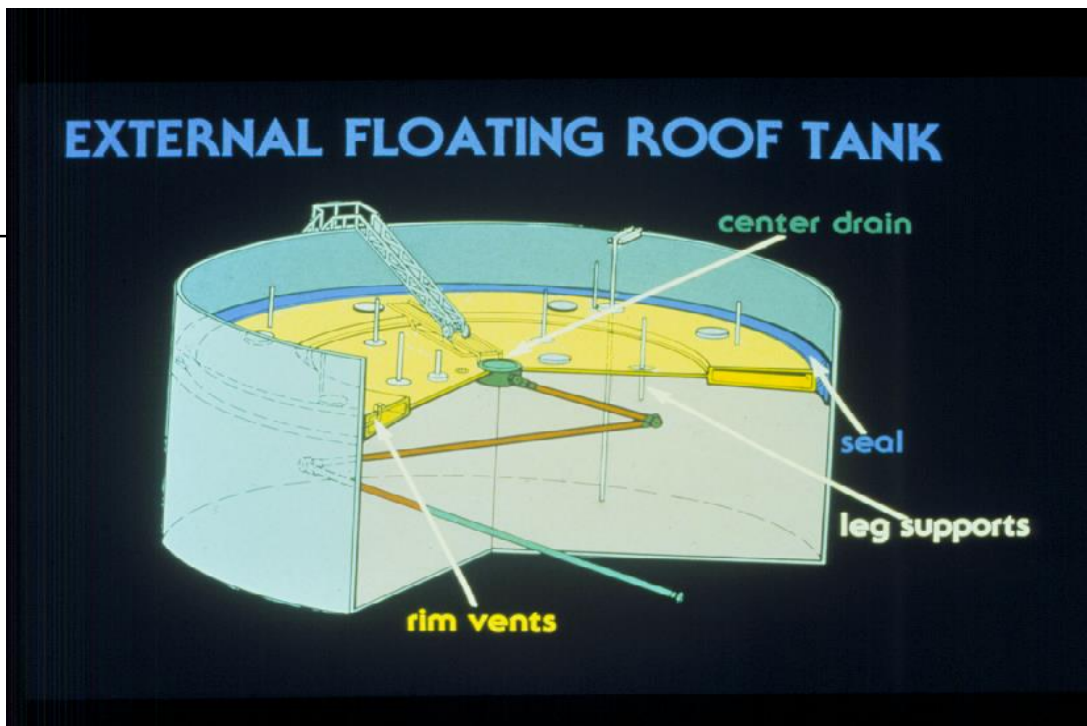
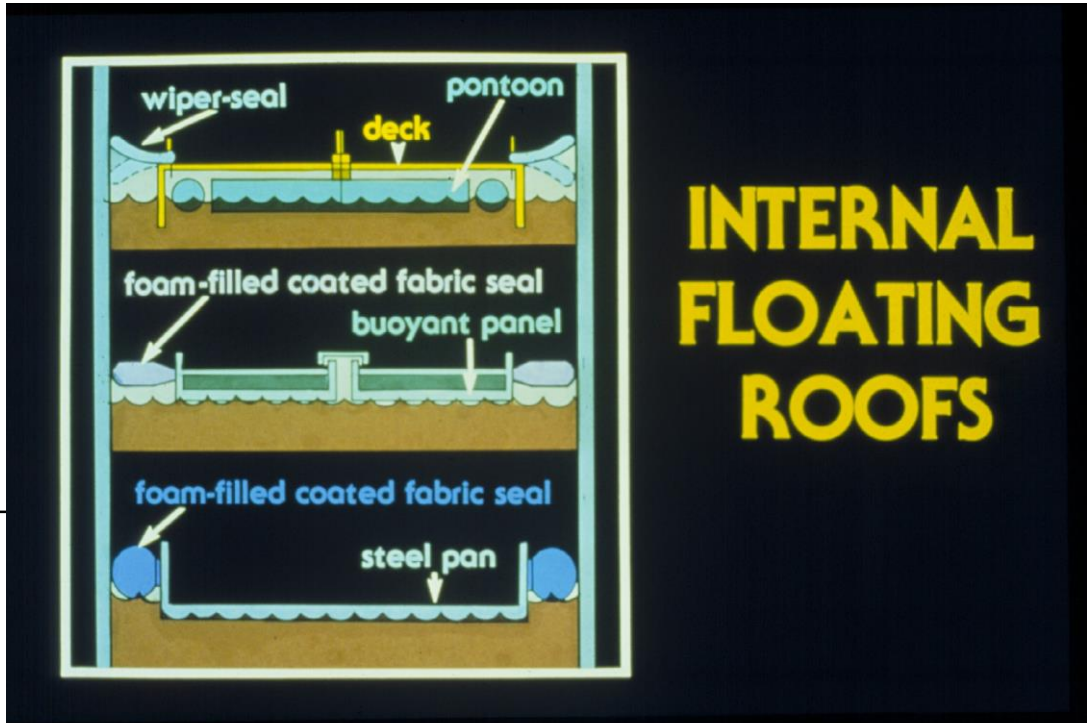


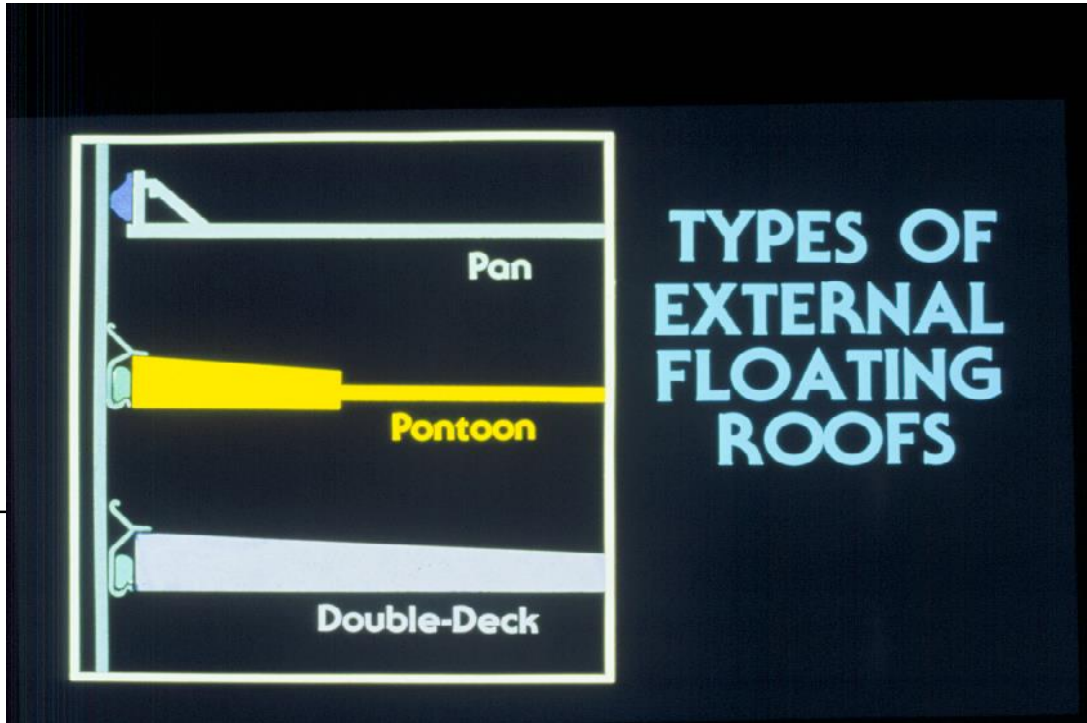


Floating Roof Tanks

- Tanks designed to have roofs that float on the liquid surface to eliminate the formation of a vapor space
- Types of floating roof tanks
 - Internal
 - External





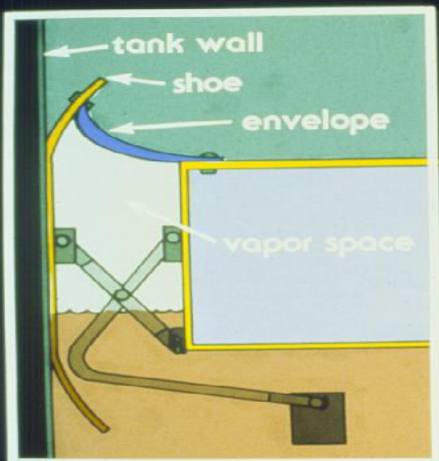


Primary/Secondary Seals

Primary Seals

Metallic Shoe Page 302-16

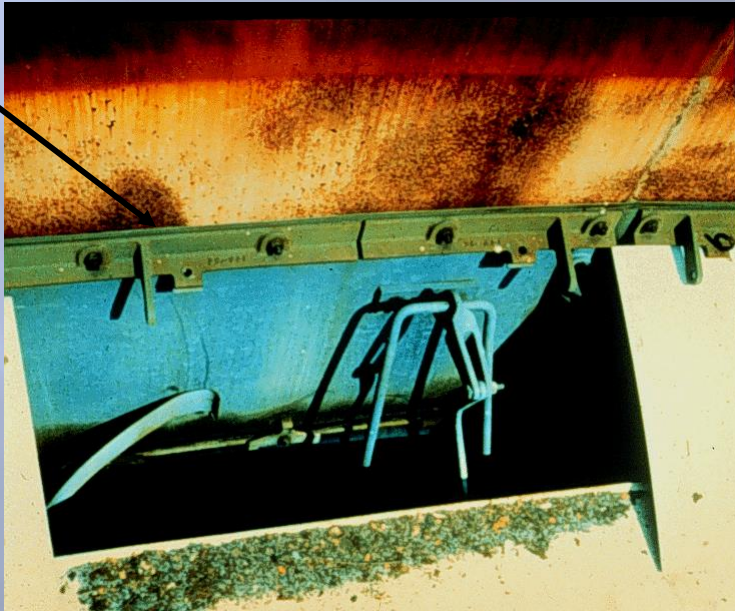
Resilient toriod Page 302-17



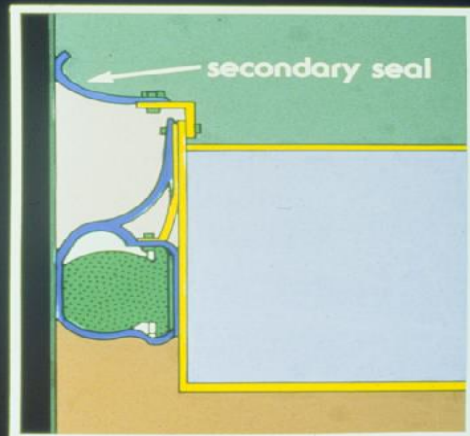
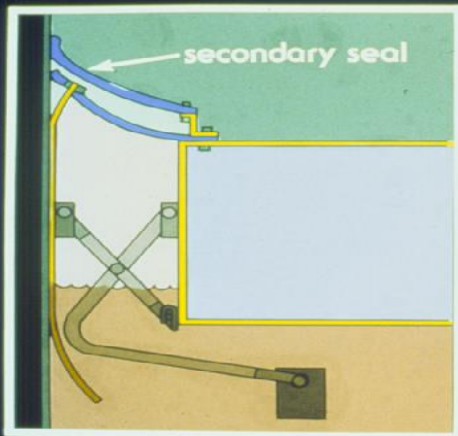
MECHANICAL SHOE SEAL

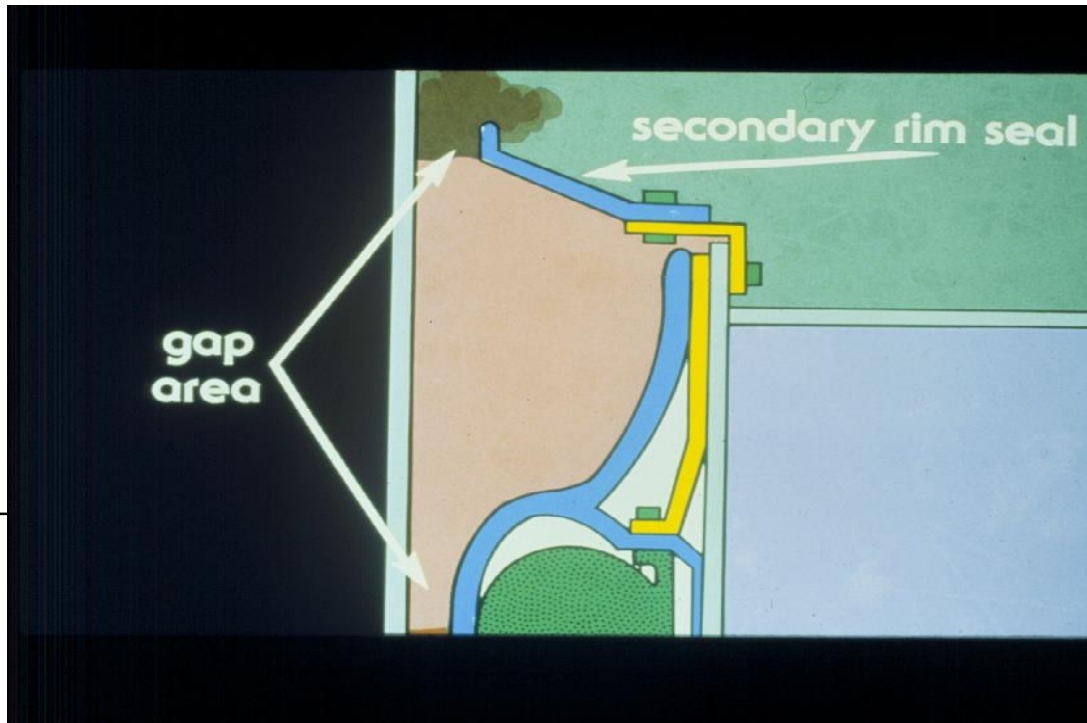
Side Wall of A Storage Tank

Primary Seal



SECONDARY SEALS





Inspection Points

- Primary and Secondary Seals
- Sample Hatch
- P/V Valve
- Level Gauge
- Water Draw
- Roof Drain/Emergency Roof Drain
- Temperature Gauges



**Checking the
Secondary Seal
on a Storage
Tank**

Sampling Hatch on Storage Tank



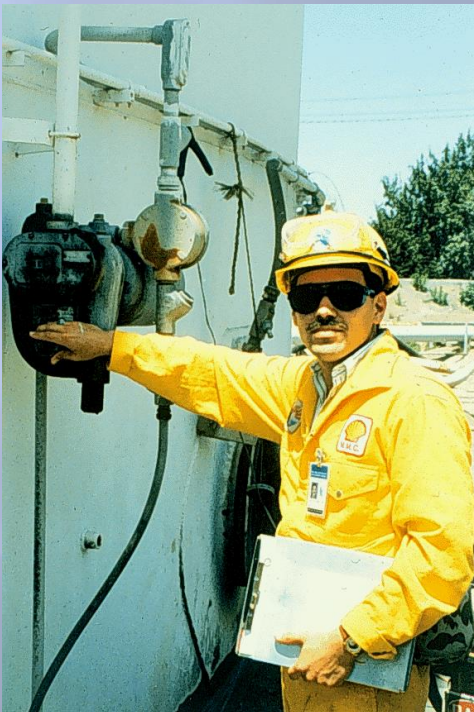


Sampling Well Inside of a Floating Roof Storage Tank



**Leg of a Floating Roof Storage Tank
- position of leg when the tank is in service**

Inside of a Floating Roof Storage Tank



Level
Gauge
for
Storage
Tank



VOC Emission Control on Floating Roof Tank

Other Equipment

- Pumps, valves, compressors - Leaks
- Reciprocating internal combustion engines
- Gas turbines
- A big emitter we'll cover later – Fluid Catalytic Cracking Unit (FCCU)



Quick Review 2

- Equipment & associated emissions
 - Fired heaters - combustion
 - Heat exchangers – fugitives due to leaks
 - Flares - combustion, fugitives, odors
 - Cooling towers - fugitives, odors
 - Vacuum jets - fugitives
 - Storage tanks - fugitives
 - Pumps, valves, compressors - fugitives
 - Internal combustion engines - combustion
 - Gas turbines – combustion
 - Don't forget about the FCCU

