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 Petroluem

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













The Oil Boom

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





Eames Petroleum Iron Works

PETROLEUM, OR ROCK OIL.

A NATURAL REMEDY

PROCURED FROM A WELL IN ALLEOHENY COUNTY, PA.

Four hundred feet below the Earth's Surface: PUT UP AND SOLD BY

STUDBT II' BIBD'

OANAL BASIN, SEVENTH STREET, PITTSBURGH, PA.

1 40 2

The healthird halos from Neares a second spring. The binnes of health, and life, to max will bring its from her depths the magin liquid flows. To calso mar scienting, and assuage our work.

CAUTION --As many persons are now going about and wending an article of a sparious character, calling it Petroleum, or Rock Gil, we would carrien the public equinst all preparations bearing that name not having the name of N. M. Kraz written on the label of the bottle.

PETROLEUM,-It is necessary, upon the introduction of a new medicine to the potice of the public, that something should be said in relation to ins powers in heating disease, and the manner in which it acts. Man's organization is a complicated out; and to understand the functions of each organ, requires the study of years. But to understand that certain remedies produce officin impressions upon three argains, stay he learned by experience in a short time. It is he deservation in watching the effects of various medicines, that we are enabled to hornast file number of cursuiva agents; and when we have discovered a new molicine and attented its mergin; if is our dairy to being is holder the public, so that the handlin so be derived from is may be more generally diffused, but have no right to hold back a settedy whose powers are calculated to remove pain and to alleviate haman 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 appealized with its virtues, doubted, its healing properties. The cry of humbug was mised against it. It had some friends,-thus that was cared through its wonderful agency. These spoke ent in in favor. The lame, shringh its instrumentality, were made to walk -- the blind, to see. These who had suffered for yours under the testaring pains of REECENTING, GOUT and NETRALOIS, were restored to health and usefulness. Several who were blind have been made to see, the evidence of which will be placed hefter you. If you still have doubts, go and ask those who have been enred! Same of them live in our mides, and ean answer for themselves. In writing about a molicine, wa are aware that we should write TRUTH-that we should make no statements that cannot be proved. We have the wirnesses-crowds of them, who will testify in terms stronger than we can write them. to the afficacy of this Remedy, who will testify that the PETROLAUM has done for them what no modicing over could before -cases that were presonned hopsless, and beyond the reach of remolinge means-cases alandoned by Physicians of unquestioned celebrity, have been made to exclaim, "THIS IN THE MOST WONDERFUL REMEDY EVER DISCOVERED! We will he before roa the certificates of score 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 Remediza. If the Physfrians do not recommand it, the people will have it of themselves -- for its transcendent pawer as head, still and must became known and appreciated-when the voices of the curvel speak out, when the curves themselves stand out in hold rolief, and when he who for years has suffered with the turtures and panys of an immedicable losing, that has been shortening his days, and hastening him "to the narrow house appointed for all the living," when he speaks out in its praise, who will doubt it! The Paraotaura rs a Naronan Regent-it is pet up as it flows from the bosom of the such, without anything being ad lad at or toleast from it.

1864 Oil Field

2010

1864 Refinery

1880 Oil Refinery

DALENKER

CONTRACT OF

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 LAR	GEST	REFIN	ERIES

Table 3

	Company	Location	Crude capa- city, b/cd
123456789011234567890112314567890	Paraguana Refining Center SK Innovation GS Caltex Corp. Reliance Petroleum Ltd. ExxonMobil Refining & Supply Co. Reliance Industries Ltd. S-Oil Corp. ExxonMobil Refining & Supply Co. Saudi Arabian Oil Co. (Saudi Aramco) Formosa Petrochemical Co. ExxonMobil Refining & Supply Co. Hovensa LLC Marathon Petroleum Co. LLC Kuwait National Petroleum Co. Shell Eastern Petroleum (Pte.) Ltd. BP PLC Citgo Petroleum Corp. Shell Nederland Raffinaderij BV Sinopec Saudi Arabian Oil Co. (Saudi Aramco)	Cardon/Judibana, Falcon, Venezuela Ulsan, South Korea Yeosu, South Korea Jamnagar, India Jurong/Pulau Ayer Chawan, Singapore Jamnagar, India Onsan, South Korea Baytown, Tex. Ras Tanura, Saudi Arabia Mailiao, Taiwan Baton Rouge, La. St. Croix, Virgin Islands Garyville, La. Mina Al-Ahmadi, Kuwait Pulau Bukom, Singapore Texas City, Tex. Lake Charles, La. Pernis, Netherlands Zhenhai, China Rabigh, Saudi Arabia	940,000 840,000 760,000 660,000 580,000 565,000 560,500 550,000 550,000 502,500 500,000 490,000 466,000 466,000 462,000 451,250 440,000 403,000 400,000
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

08 788

DANGEROUS EXPLOSIBILITY

PETROLIUM, COAL OILS,

CAMPHENE, SALT - PETRE, &c.

(from the lateral Report of the Southernian Southering in the year (98) (1)

BY EACHARIAS ALLES.

PROVERSION : SECOND & REDAR, 17 WINFORDERS STREET, 1995

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

- **NOx Combustion Sources**
 - Fired Heaters (70%)
 - Fluid Catalytic Cracker (10-15%)
- SOx 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

- $C1 = Methane (C_1H_4)$
- $C2 = Ethane (C_2H_6)$
- $C3 = Propane (C_3H_8)$
- $C4 = Butane (C_4H_{10})$
- $C5 = Pentane (C_5 H_{12})$
- $C6 = Hexane (C_6H_{12})$
- $C8 = Octane (C_8H_{18})$ Octane Rating
- C16 = Cetane ($C_{16}H_{34}$)- Cetane Rating

Physical Properties

- Boiling point
- Structure
- Reactivity
 - ExothermicEndothermic

Physical Properties					
NAME	FORMULA	BOILING POINT			
Methane	CH_4	-162			
Ethane	C_2H_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

 \frown

PENTANES (Paraffin)

C-C-C-C

62 Octane

> 120 Octane

C-C-C

80 Octane

Cracking Expansion

 $C_{16}H_{34}$

 C_2H_4 **C**₆**H**₁₂ C_8H_{18}

7.2 lbs 1 gallon 7.2 lbs1.3 gallons

ANS CRUDE BLEND REPORT FOR WEEK ENDING NOV 20, 1987

CRUDE PROPERTIES

Crude Oil	
Assay	

Assay Gravity Sulfur, wt% Nitrogen, ppm Concarbon, wt % Nickel,ppm Vanadium, ppm CRUDE BLEND DATA Defined Components Am	nalysis			27.1 1.16 2009 4.79 12 26 Vol%
C2				
C3				0.04
iC4				0.33
nC4				1.53
iC5				0.81
nC5				1.14
C6+				95.71
Total				100.00
TBP	API	Sulfur	Diff	Cum
Distillation	Grav	Wt%	Vol %	Vol %
C4-	124.0	0.00		
150 F	74.7	0.00	2.4	2.4
200 F	59.6	0.00	2.4	5.9
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	5.5	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
800 F	20.9	1.34	4.3	65.1
950 2	19.5	1.49	4.0	69.1
1000 -	17.6	1.64	4.2	73.3
1050 5	16.0	1.80	4.0	11.3
1100 5	13.6	1.89	3.9	81.2
1100+ 2	11.4	1.97	3.6	100.0
	4.9	2.42	13.4	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

-Crude Distillation

- -Hydrotreating of Middle Distillation
- -Catalytic Reforming of Naptha

Complex-Simple Plus

- -Vacuum Distillation
- -Catalytic Cracking
- -Alkylation Plant
- -Gas Processing

Very Complex -Olefin Unit -Complex Plus -Residue Reduction (Coker)

TORRANCE REFINERY

Simple Refinery



SIMPLE REFINERY



Complex Refinery



Very Complex Refinery



Complexity and Yields

Fuel Type	<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



ProcessHeaters

Cabin Type

Upright Type





Multi-Pass Process Heater



Emissions From Boilers/Heaters



H₂O CO₂ CO NOX HC SOX PM CHO

Types of Fired Heaters

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





Combustion Air Preheat





Stack Damper on **Natural** Draft Heater





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 NOx vs. Temperature



Graphic Courtesy of Coen

NOx Control Methods

Pages 201-207

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


Flue Gas Recirculation (FGR)



FGR Impact







Figure 201.5 Low-NOx Burner with Staged Fuel and Internal Flue-Gas Recirculation



Figure 201.6 Low-NOx Burner with Staged Fuel and Steam Injection



Low NO_x Burner





Low NO_x Burner Flames











Selective Catalytic Reduction (SCR)

NOx control thru ammonia (NH₃) injection $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$ $2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$ 65-90% control Catalyst **Problems** NH_3 **Expensive** X NH3 **High maintenance** O→ H₂O $\longrightarrow N_2$ NO, Ammonia "slip" Flue O→ H₂0 Gas NO. $\rightarrow N_2$ **Catalyst replacement** X NH3 O→ H₂0 & disposal



Figure 201.2 Gas-Fired Heater With Retrofit SCR System

Selective Catalytic NO_x Reduction (SCR)





Ammonia Injection System for SCR

Selective Non-Catalytic Reduction

NOx 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

Catalyst

Problems:

Changing flue temperatures with changing load Formation of ammonium salts Ammonia slip





ANHYDROUS AMMONIA

3 0

ANHYDROUS

AMMONIA

IDANGER NO SMOKING, MATCHES OR OPEN LIGHTS

NE 1

10

10

D

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





Wet FGD Scrubber

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 tomorow

Flares Continued

REGULATIONS:
Visible Emission Evaluation (VEE)
Odors
SOx



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)



Purpose: Use air to cool or condense process streams



Heat Exchangers Used in Conjunction with Air Coolers



Heat Exchangers





Figure 304.2 Heat Exchanger (Simplified)

INLET

Heat Exchanger Bundle









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:Utube_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





Figure 304.1 Simplified Cooling Tower

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.



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)




Figure 302.2 Fixed Roof Tanks With Vapor Recovery

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





INTERNAL FLOATING ROOFS

EXTERNAL FLOATING ROOF TANK





TYPES OF EXTERNAL FLOATING ROOFS

Primary/Secondary Seals

Primary Seals

Metallic Shoe Page 302-16

Resilient toriod Page 302-17



MECHANICAL SHOE SEAL

Side Wall of A Storage Tank



SECONDARY SEALS







Inspection Points

- Primary and Secondary Seals
- Sample Hatch
- P/V Valce
- 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

