

How to Treat Refinery Gases And Make Them Suitable to Recover Valuable Liquids

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ABSTRACT

Refinery Fuel Systems are generally a mixture of Gases coming from several different units within the refinery. The quantity and quality of gases in the fuel system depends on refining capacity, severity of cracking unit and the quality of refinery crude. Some US refineries are long on fuel and this excess fuel is flared. Despite being flared, this fuel gas contains several valuable components like hydrogen, ethylene, propylene, propane and higher olefins. These components can be recovered economically from the fuel gas. By not flaring these components, Refineries reduce their emissions and contribute to the margins. This paper addresses how to treat refinery gas to meet the product specifications for the polymer grade ethylene and propylene. This paper also address how each contaminant is removed from the fuel gas, the reason for its removal, the chemistry and engineering involved

If the desired recovery is C₃+ components then minimal treatment of the fuel gas is required (Amine and Dehydration), however if C₂+ recovery is desired, treatment requirement become complex and expensive. Regardless, the treating strategy must address Product Specifications and Safety.

Introduction

Refinery off-gas (ROG) comes from a variety of units within the refinery. The quality and quantity of the ROG is dependent on the type of crude and the complexity of the refining. The majority of the fuel gas stream is generated In Fluidized Catalytic Cracking Unit (FCC) where the long chain hydrocarbon molecules are broken into lower molecular chains or lighter hydrocarbon components. Significant amounts of olefins are also produced during hydro-treating. These olefins are valuable and can increase revenue. Often the refinery off-gas also contains a large amount of hydrogen that, if recovered, can provide economic value. Hydrogen can be recovered either utilizing pressure swing adsorption (PSA) or cryogenic process.

Table I illustrates the range compositions of the ROG components. Table II reflects the refinery gases contaminants. Several of the contaminants have to be removed from the feed gases, either to meet product specifications (shown in Table III) or to mitigate the operational hazards.

After removing the hydrocarbon liquids the residual gases are an excellent feed stock for a hydrogen plant utilizing steam methane reforming technology.

In order to prepare the gases for ethylene liquids recovery the following contaminants must be removed in order to meet the product specification listed in Table III trough VII.

1. Hydrogen Sulfide (H₂S) and Carbon Dioxide (CO₂)
2. Ammonia
3. Chlorides
4. Water
5. Mercury
6. Carbonyl Sulfide (COS)
7. Arsine

8. Acetylene
9. NO, NO₂, NO_x (Nitro Gum)
10. Dienes (1-3 butadiene , acetylene , propadiene etc.)

The composition of the ROG gas depends on the type of crude, the cracking severity and type of catalyst used for cracking. Typically, range of components in the FCC gas is listed below in Table I the trace components are listed in Table II :

Table I

Typical FCC off-gas Composition

Component	Mol %
Hydrogen	10-50
Carbon Monoxide	0.1-1
Nitrogen	2-10
Methane	30-55
Ethylene	5-18
Ethane	15-20
Propylene	1-6
Propane	1-6
Butadiene	0-0.15
Butylene	0.1-0.5
Iso & N-Butane	0.5-1
C ₅ ⁺	0.2-2

Before a treating system can be designed, several trace components must be properly analyzed. These components are listed in Table II below. There are several laboratories around the U.S. that can analyze these components accurately. The concentration of the components shown in Table II is dependent on refinery complexity and type of the crude.

Table II
Refining off-gas Contaminants its Method of Analysis and Expected Concentration

Component	Preferred method of Analysis	Detector Tube Available?	Expected Concentration
Hydrogen Sulfide	Titrator	Yes	25 ppmv
Carbon Disulfide	Titrator	Yes	1 ppmv
Sulfur Dioxide	Mass Spec	Yes	1 ppmv
Methyl Mercaptan	Titrator	Yes	700 ppmv
Ethyl Mercaptan	Titrator	No	120 ppmv
Propyl Mercaptan	Titrator	No	50 ppmv
Dimethyl Disulfide	Titrator	No	10 ppmv
Methyl Sulfide	Titrator	No	5 ppmv
Carbonyl Sulfide	Chromatograph	Yes	50 ppmv
Other Mercaptans	Titrator	Yes	50 ppmv (Total mercaptan test)
Carbon Dioxide	Chromatograph	Yes	400 ppmv
Ammonia	Chromatograph	Yes	500 ppmv
Arsine	Mass Spec	Yes	1 ppmv (normally in ppb range)
Acetylene	Chromatograph	Yes	Trace < 500 ppmv
Methyl-Acetylene	Chromatograph	No	Trace
Mercury (all forms)	Altec Absorption Method	Yes	10 ppmv
Lead	Mass Spec	No	200 ppmv
Propadiene	Chromatograph	No	< 1mole percent
Butenes (2)	Chromatograph	No	< 1mole percent
Butadiene	Chromatograph	No	< 1mole percent
Pentadiene	Chromatograph	No	< 1mole percent
Benzene	Chromatograph	Yes	< 1mole percent
Toluene	Chromatograph	Yes	< 1mole percent
Xylenes	Chromatograph	Yes	< 1mole percent
Hydrogen Cyanide	Mass Spec	Yes	< 100 ppmv
Nitric Oxide	Mass Spec	Yes	< 500 ppmv
Nitrogen Dioxide	Mass Spec	Yes	< 500 ppmv
Oxygen	Chromatograph	Yes	< 1mole percent
Carbon Monoxide	Chromatograph	Yes	< 1mole percent
Methyl Acetate	Mass Spec	No	120 ppmv
Alcohols	Mass Spec	Yes	50 ppmv
Aldehydes	Mass Spec	No	100 ppmv
Ketones	Mass Spec	Yes (acetone)	100 ppmv
Bitumen	Unknown	No	Unknown
Amines	Mass Spec	Yes	< 500 ppmv

Notes:

1. Mercaptans heavier than propyl and can be grouped as total mercaptans
2. The butene analysis should be specific for N-Butene, Isobutene, Trans-2-Butene, Cis-2-Butene, 2-Methyl-1-Butene, 2-Methyl-2 Butene, 3-Methyl-1-Butene
3. The above compounds are contaminants from a product specification viewpoint. Other compounds such as Hydrogen Sulfide, Carbon Dioxide, Mercury, Butadienes, Pentadienes, Nitric Oxide and Oxygen also have a potentially negative affect from a safety or equipment viewpoint. Therefore, these components must be identified regardless of the product specifications.

4. Sodium, Chlorides and Fluorides may be present in trace quantities

The prospective products of the refinery liquid recovery units are:

1. Ethylene
2. Ethane
3. Ethylene/Ethane Mix
4. Propylene
5. Propane
6. Gasoline or C₅+
7. Residue Gas or Fuel Gas

The product specification is dependent on the market requirement for product sales.

Table III below lists typical product specifications for a chemical and polymer grade ethylene.

Table III

Typical Ethylene Product Specifications

		Chemical Grade	Polymer Grade
No	Composition		
1	a. Ethylene, minimum, mol %	99.5	99.85
	b. Ethane, maximum, ppmv	1,000	400
	c. Propane, maximum	--	--
	d. Propylene, maximum, ppm-mol	10	10
	e. Carbon Dioxide	50 ppmv	5 ppmv
	f. Methane, maximum	500 ppmv	0.15% by vol
	g. Acetylene, maximum	5 ppmv	5 ppmw
	h. Moisture, maximum	2	1 ppmv
	i. Ammonia, maximum, ppbw	10	0.5 to 1
	j. Carbon Monoxide, maximum ppmv	10	0.5
	k. Carbonyls, maximum, ppmw	--	5
	l. Hydrogen, maximum, ppmv	--	1
	m. Methanol, maximum, ppmv	--	5
	n. Oxygen, maximum, ppmv	20	5
	o. Total Sulfur, maximum, ppmw	--	1
	p. Total Chlorides, ppmv	--	1
2	Corrosiveness		
	Copper strip at 100 F	No. 1	--
3	Volatile Sulfur, ppmv	10	
4	Water Content, maximum, ppmv	10	0.5 to 10

Ethane sold as an ethylene cracker feed stock must meet certain purification .Table IV below lists typical specifications for the ethane minimum feed stock:

Table IV

Ethane Product Specifications

No	Specification	Field Grade	Cracker Feed
1	Composition		
	a. Ethane, maximum, mol %	95	99
	b. Carbon Dioxide, ppmw	500	1
	c. Methane, maximum	3.0 mol %	150 ppmw
	d. Ethylene, maximum, ppmw	NA	1
	e. Propane Plus, maximum	3.5 mol %	1 ppmw
	f. Acetylene, maximum, ppmw	NA	1
	g. Olefins, maximum, ppmw	NA	1
	h. Aromatics, maximum, ppmw	NA	1
	i. Ammonia, maximum, ppbw	1	1
	k. Arsine, ppmw	10	10
	l. Phosphene, ppmw	10	10
2	Corrosiveness	No. 1	No. 1

Propylene may be sold as chemical, refining and polymer grade. Propylene is separated from propane using C₃ splitter fractionation. Table V below lists chemical and refining grade while Table VI given below gives a polymer grade product specification.

Table V

Chemical and Refining Grade Propylene Product Specifications

No	Specification	Chemical Grade	Refining Grade
1	Composition		
	a. Propylene, minimum, LV %	99.5	60-65
	b. Carbon Dioxide, ppmw	1	
	c. Methane, Ethylene, Ethane, maximum, LV%	0.5	1.5-2.25
	d. Propane, maximum, mol %	0.5	Remaining
	e. Butanes, Butenes LV %		0.5-1.00
2	Corrosiveness		
	Copper strip at 100 F	No. 1	
3	Volatile Sulfur, ppmw	185	
4	Dryness	No water	No water

Table VI

Polymer-Grade Propylene Production Specifications			
Component	Unit of Measure	Export Spec	PPBW Spec
Propylene	wt %	99.5 min	99.45 min
Propane	wt %	0.4 max	0.55 max
Hydrogen	wppm	1 max	1 max
Methane + Ethane	wppm	200 max	350 max
Ethylene	wppm	10 max	10 max
Acetylene	wppm	1 max	1 max
Methyl Acetylene	wppm	1 max	1 max
Propadiene	wppm	1 max	1 max
1,3 Butadiene	wppm	1 max	1 max
Butanes + Butylenes	wppm	10 max	10 max
Water	wppm	2 max	2 max
Oxygen	wppm	1 max	1 max
Methanol	wppm	1 max	1 max
Carbon Monoxide	wppm	1 max	3 max
Carbon Dioxide	wppm	3 max	5 max
Arsine	wppb	20 max	20 max
Carbonyl Sulfide (COS)	wppb	20 max	20 max
Elemental Sulfur	wppb	500 max	500 max

Table VII below gives a HD-5 grade propane specification.

Table VII

HD 5 Grade Propane Specifications

No	Specification	HD-5 Grade
1	Composition	
	a. Propane minimum, Liquid vol %	90
	b. Butane and heavier, Liquid vol %	2.5
	c. Pentanes and heavier	None
	d. Temperature at 95% evaporation, °F	-37
2	Vapor Pressure at 100 °F, max	208 psig
3	Corrosiveness	
	Copper strip at 100 °F	No. 1
4	Volatile Sulfur, ppmw	185
5	Dryness	No water

CONTAMINANT REMOVAL

A. Mercury Removal

Mercury is present in natural gas, natural gas associated condensates and in refinery off gases, as organometallic and inorganic compounds, and in the elemental (metallic) form depending on the gas source. The elemental form can be found in either the vapor or liquid phase. The organometallic (typically dimethyl mercury, methylethyl mercury, or diethyl mercury) and in an inorganic form (such as HgCl_2) mercury condense into the liquid phase in any hydrocarbon fractionation column. Vapor-phase elemental mercury is a primary source of corrosion in aluminum heat exchangers.

Elemental mercury that leaves the plant with the hydrocarbon liquid streams is a primary source of corrosion for the aluminum equipment in olefins liquid recovery plants. Mercury also poisons the selective hydrogenation catalysts in olefin plants, and can pose inhalation hazards to workers.

The organometallic and inorganic forms mercury usually ends up in the condensate stream from the natural gas or refinery liquid recovery plant. These compounds are important environmental toxins that are easily absorbed and accumulated by biological organisms. The presence of these compounds in gas condensate streams leads to waste disposal problems and safety hazards to workers.

Although relatively high levels of elemental mercury were discovered in the Groningen (Holland) field as early as 1969, the first recorded cold box failure attributed to mercury corrosion was in the aluminum spiral wound heat exchanger of the LNG plant at Skikda, Algeria, ¹ in 1974. Since this time, mercury in natural gas has become a major concern in cryogenic gas processing industries. These industries, or refinery gases including liquefied natural gas (LNG), liquefied petroleum gases (LPG), and olefins recovery, often use Brazed aluminum heat exchangers in their cold boxes. Mercury corrosion of aluminum exchangers has led to several additional failures since the problems at Skikda. In addition, mercury accumulation can lead to poisoning of catalysts used in olefin processes, personnel safety hazards, and waste disposal difficulties

Mercury Sources

Elemental mercury is a natural contaminant present in the produced natural gas in various concentrations at certain geographic locations. The concentration of elemental mercury in the gas stream is often expressed in $\mu\text{g}/\text{Nm}^3$, which is a very small number. Generally speaking, elemental mercury levels have been found to be the highest in Southeast Asian gases (up to $400 \mu\text{g}/\text{Nm}^3$ in the vapor phase) and lowest in United States Gulf Coast gases (as low as $0.02 \mu\text{g}/\text{Nm}^3$), although wide variation is known to occur even within local regions. However, even at the very lowest natural concentrations it is still desirable to reduce the amount of mercury before any cryogenic processing, either in refinery or natural gas streams. The Mercury can accumulate to higher concentrations over time.

The mechanism for the formation of organometallic mercury is not known. Current theory suggest that elemental mercury may react with the walls of reboilers and catalytic furnaces to form active species which can then react with methane, ethane, ethylene, the products of a ROG Gases, and other organic compounds.

How to Remove Mercury

Mercury is removed from LPG plants to protect the aluminum heat exchangers from corrosion. Sulfur-impregnated activated carbon is used to remove mercury from the gaseous hydrocarbon feed stock. Mercury removal by the activated carbon is much more efficient if the moisture is not present or removed from the stream before coming in contact with activated carbon. The maximum attainable mercury concentration in the treated gas stream is not pressure dependent. A typical mercury removal system is shown in Figure 1.

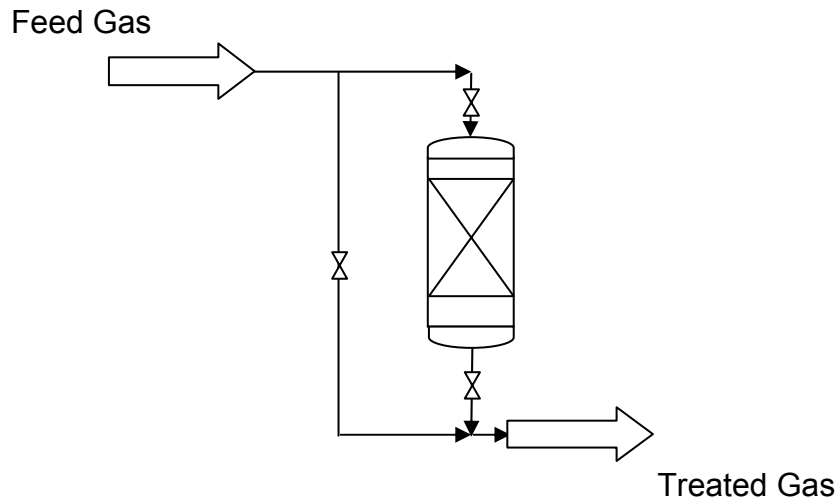


Figure I Typical Mercury Removal System

The mercury removal process can be a single or dual bed adsorption system. The system can be designed to reduce mercury to a concentration of $< 0.01 \mu\text{g}/\text{Nm}^3$. The chemical reaction converts the mercury to mercuric sulfide. The sulfide product is then retained in the pores of the carbon granules. The mercury capacity of the activated carbon can be 15-20% by weight.

Activated Carbon Specification

Density,	Approximately 37 lb/ft ³
Sulfur content by Weight	10%

B. Arsine

The presence of an arsine compound (AsH_3) in a hydrocarbon stream may act as a poison for the selective hydrogenation catalyst. The presence of arsine is a specific problem in C_2 splitter column since its boiling point is between ethane (C_2) and ethylene ($\text{C}_2 =$) it tends to build up in the column without leaving either with overhead or bottoms product.

Arsine is generally present in the refinery gases in the concentration of less than 1ppm . This small quantity is enough to poison the selective hydrogenation catalyst.

A sacrificial bed either filled with ZnO or CuO material is use to retain arsine (AsH3). Arsine removal material is available from several different catalyst suppliers.

C. COS (Carbonyl Sulfide)

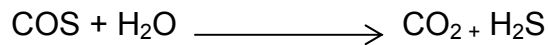
Traditional treating with caustic or amine solution is not effective in removing COS (carbonyl sulfide) from a hydrocarbon stream.

COS can be removed from the refinery off gases by the following two ways:

1. COS removal by hydrolysis
2. COS removal by adsorption (in our opinion this is a better approach)

COS Removal by Hydrolysis

There are several catalysts available to hydrolysis the COS into H₂S and CO₂ by the following reaction.



Some catalysts perform both the hydrolysis of COS to the reaction products H₂S plus CO₂ and the subsequent retention of both these acidic compounds (H₂S and CO₂)

These catalysts may be used for the purification of either liquid or gas streams. The stream to be purified must contain equilibrium water (typically 300 ppmw) but must not contain free water which would destroy the material. These catalysts do not require activation before use.

Typical operating conditions for hydrolysis catalyst are.

Temperature -----100-250°F

Pressure -----150-440 psig

COS Removal by Adsorption

The COS removal by adsorption is done on the dry feed gas. The system is very similar to a molecular Sieve dehydration system. Two beds with switching valves are

installed one bed is in adsorption mode while the other is regenerated and cooled. The system usually has a cycle time of 168 hours (one week) while the offline bed can be heated for 5 hours and cooled for 4 hours and the rest of the time is a standby time. The system requires a regeneration temperature of 550°F and generally the dry fuel gas is used to regenerate the beds. The regenerated fuel gas containing the entire COS can be returned to the refinery fuel system. A typical system is shown in the Figure II.

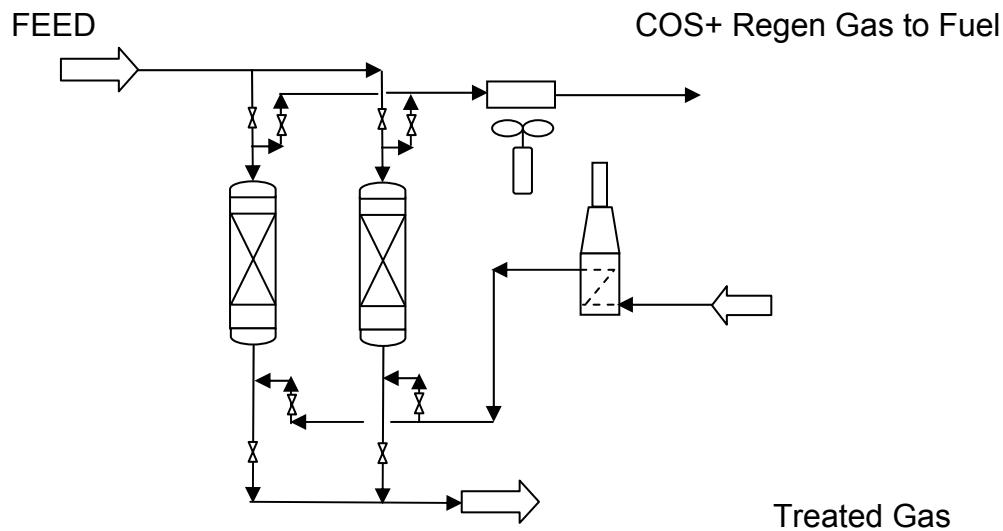


Fig II Regenerative Type COS Removal System

D. Hazards of Nitrous Oxide Accumulation in Cryogenics Olefins Recovery Units

1. Sources of The NO_x Compounds

NO_x is found in FCC gases. NO_x is produced during combustion of the coke on the FCC catalyst in the FCC regenerator. Some flue gas from the regenerator is entrained into the reactor with the recirculation catalyst, together with oxygen and nitrogen, where these light gases comingle with gases produced in the FCC reactor and is carried forward to the FCC light ends recovery units. When C₂+ recovery for FCC off gases is practiced, the nitrogen, oxygen, and NO_x may be

Accumulated into the coldest section of the recovery facilities. Variations in FCC plant operating conditions may have a major effect on the concentration of NO_x in FCC gases.

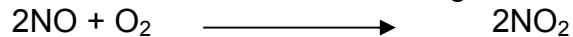
The design of Coker unit (relation of the regenerator-coke burner and the reactor) is similar in concept to an FCC unit. Thus, Coker gas, if fed to C2+ recovery unit, may be another source of NO_x.

While other sources of NO_x in feeds to ethylene recovery units may exist, the only identified source is FCC gas, and by analogy, fluid coker gas.

2. Theory and Chemistry of NO_x Accumulation in the Cold Train at Cryogenic Conditions

While other NO_x compounds exist, the principle compounds are produced by the following reaction mechanism:

NO is oxidized to NO₂ according to the following reaction:



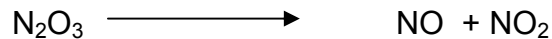
(The above reaction requires excess O₂ at low temperature but is a slow reaction)

- Equilibrium favors formation of NO₂ at low temperatures and high pressures.
- Reaction rate actually increases at low temperatures.
- Conversion of NO to NO₂ is expected to be highest at temperatures below -100°C (-148°F)
- NO further reacts with NO₂ to N₂O₃ as per the following reaction :



(The above reaction requires cryogenic temperature and high pressure)

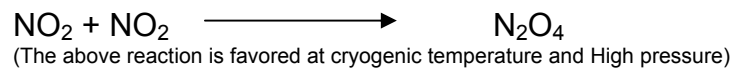
- N₂O₃ accumulation is most likely to happen in the areas of the plant where the temperature is -125°C (-193 °F) or below.
- Upon warm up the N₂O₃ rapidly disassociates according to the following reaction:



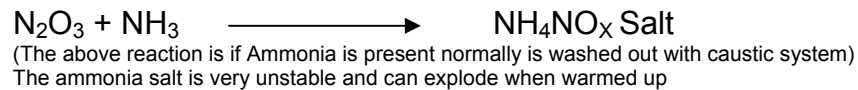
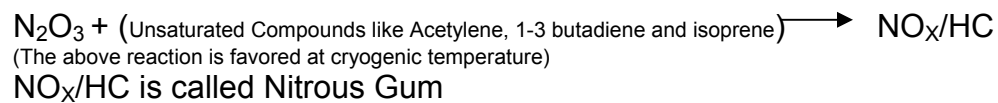
NO₂ is very toxic to humans 100 ppm exposure of NO₂ can cause pulmonary edema or death.



NO₂ Gas Collected in a Bag. The gas is Radish Brown in Color



- Dienes- also known as Diolefins, have two carbon-carbon double bonds. Diolefins such as 1,2-butadiene or 1,3-butadiene are most problematic Diolefins.
- Alkynes-is another class of unsaturated hydrocarbon, it has carbon-carbon triple bond within the molecule. Examples of alkynes are acetylene, butadiene, propadiene etc. These compounds are more reactive than paraffin's or naphthenes and readily combine with other elements such as hydrogen, chlorine and bromine



Formation of nitrated hydrocarbons can be described below:

- NO₂ reacts exothermally with olefins and diolefins forming nitrated gums (NO_x gums)
- Gums of different olefins / diolefins have different decomposition temperatures.
- NO_x gums of conjugated diolefins form very rapidly at cryogenic temperatures.
- NO_x gums of conjugated diolefins are highly unstable at cryogenic temperatures.
- NO_x gums are soluble in cold methanol (MeOH)

Nitrous gum at cryogenic temperatures is accumulated in the coldest sections of the plant (aluminum heat exchangers) and whenever the plant is warmed up the

nitrous gum decomposes at a rapid rate and is known to cause explosion and damage the equipment. A picture of the heat exchanger core damaged by such an explosion is shown below.



Brazed Aluminum Exchanger core damaged due to Nitrous gum explosion.

Key properties of these materials and some other compounds of interest are summarized in a table VIII below which also includes a vapor pressure curve for N_2O_3 (2) is shown in Figure 2.

Figure 2

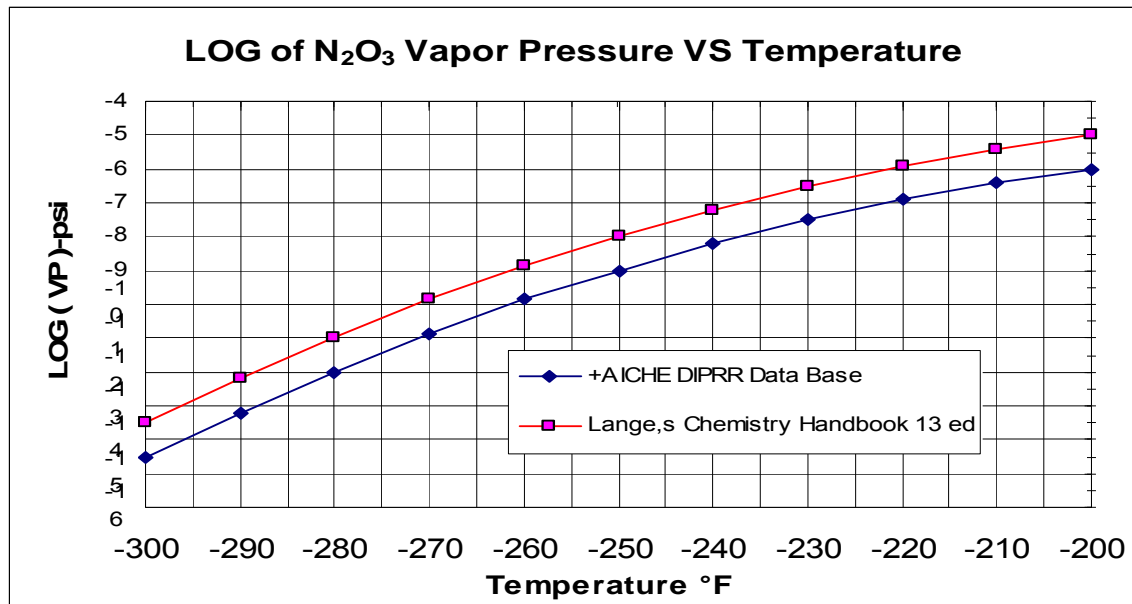


Table VIII

Physical Properties of different NOX Compounds (2)

	NO	NO ₂	N₂O₃	NH ₄ NO ₂	NH ₄ NO ₃
Melt Point	-258°F -161°C	+15.3°F -9.3°C	-152°F -102°C	+140oF +60oC (explodes)	+338°F +170°C
Boiling Point	-240°F -151°C	+69.8°F +21°C	+38.3°F +3.5°C (decomposes)		+410°F +210°C
Appearance	Colorless Gas	Red-Brown Gas	Blue Oil	Solid white Crystals	Solid Colorless Crystals

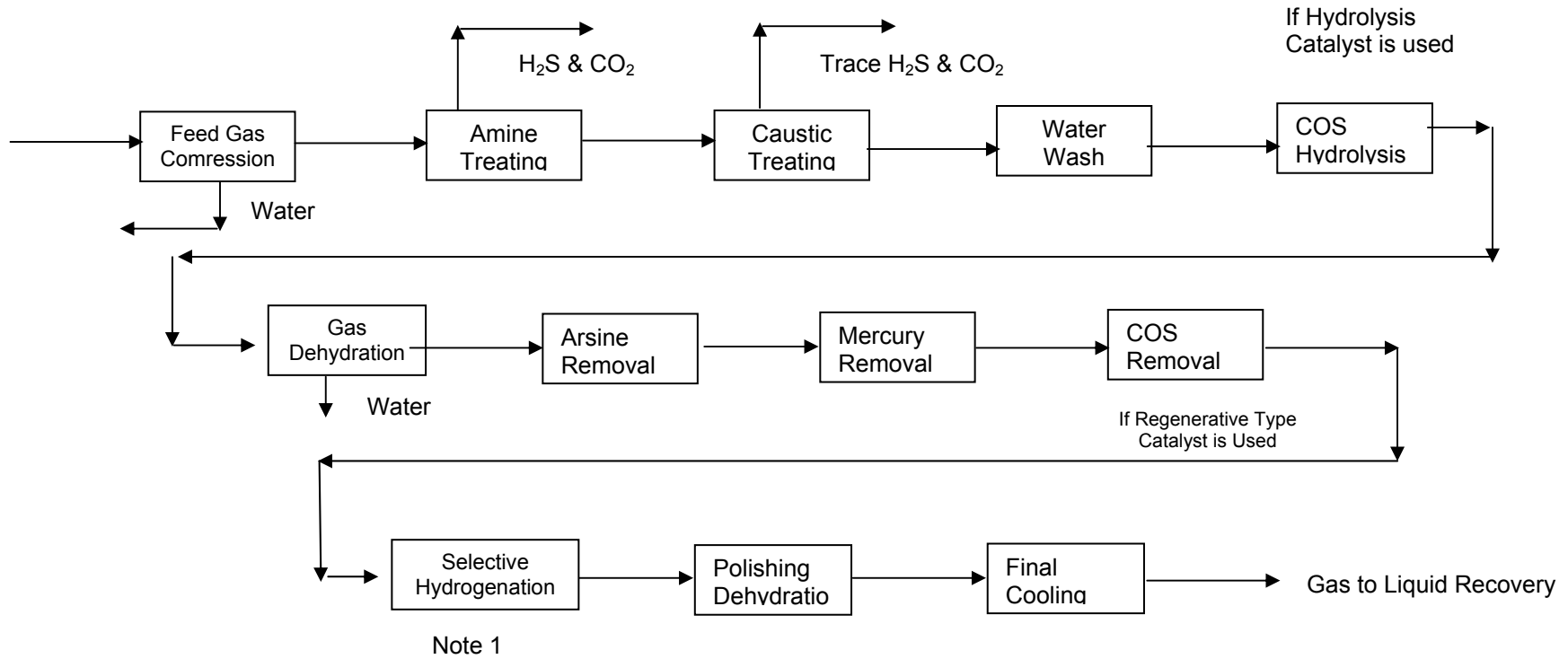
- Both NO₂ and N₂O₃ are solid at deep cryogenic temperatures.
- Solubility of NO₂ and N₂O₃ in hydrocarbons is expected to be low.
- Therefore NO₂ and N₂O₃ can freeze out and deposit in coldest section of the plant.

- A significant deposit of both NO_x and NO_x Salts has been measured in colder sections of ethylene plants.
- N_2O_3 can also react with NH_3 to Form NH_3NO_x salts which are also very unstable salt. Generally caustic treating followed by water wash can remove NH_3 from the feed Gas.

How to Reduce the Risk Posed BY NO_x Gums & Salt (1)

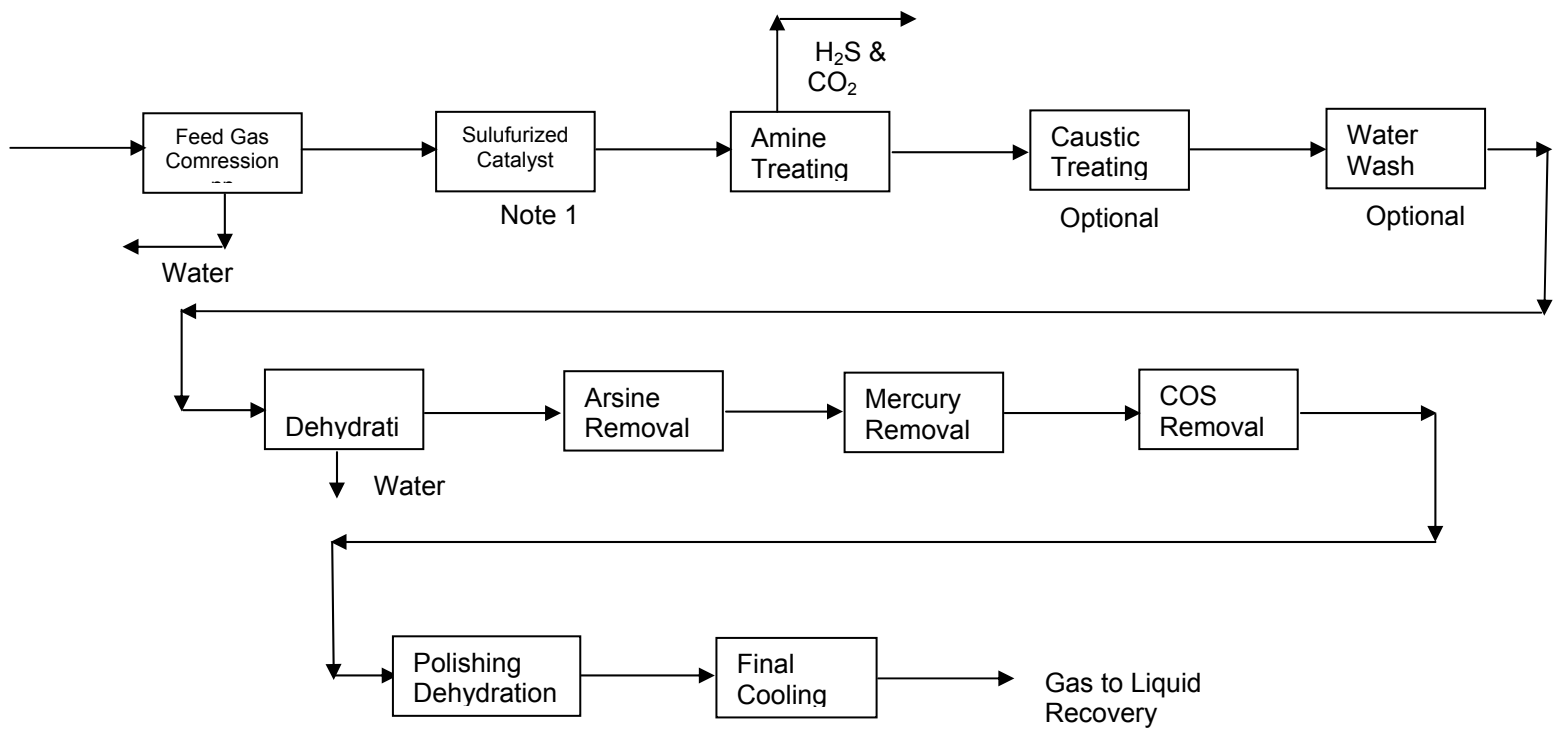
1. Refinery off-gas contains Hydrogen and H_2S . Use of Nickel sulfide catalyst (NiS) will essentially convert 100% of oxygen to H_2O . Since the oxygen is an essential element in formation of the Nitro gums and salts. The risk of explosion is minimized. NiS catalyst requires the small amount of H_2S to keep the catalyst active a small amount of H_2S in feed take care of it.
2. One alternate to the above is to convert all the triple bond components like acetylene and dienes to their olefinic form by the use of podium catalyst. This requires an extensive feed gas treatment since any form of sulfur is poison to the polonium catalyst complete removal of all sort of sulfur is essential.
3. Another alternate is not to provide any kind of treatment but build a methanol (MeOH) wash system. Periodically when you see higher pressure drop across the cold equipment the unit is shut down for a short period of time and flushed with methanol to remove all the gums and salts because their solubility in methanol is very high.

Figure 6 Typical Treating Block Flow Diagram If Non Sulfurized Based Catalyst is Used.



Note 1. Acetylene, 1-3 butadiene and other Triple Bond Components are Saturated to Double Bonds

Figure 7 Typical Treating Block Flow Diagram If Sulfurized Based Catalyst is Used.



Note 1. Acetylene, 1-3 butadiene and other Triple Bond Components are Saturated to Double Bonds also Oxygen is converted to Water essentially 100 %

The data presented in this paper is collected by the author over the years from various sources and working on different projects.

Authors are also thankful to Linde and its management for providing him with the resources and dedicate his time to write this paper.

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