Risk Assessment of Nox gums & salts in COLD Box of olefin plants & step forward

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Abstract:

Various type of impurities are integral part of feed in olefins plants. It may be in fraction or in measurable quantities. There are nitrogenous based impurities, which can react with hydrocarbons during the process of manufacturing the olefin products and convert themselves to explosive hydrocarbon & remain unnoticed. Nox in olefin feed which react with hydrocarbon to form various type of gums & salts. It acquire some space in cold box of olefin plant due to favorable condition of temperature & pressure. This paper emphasis on risk associated with Nox and categories risk as per feed & impurities. Moreover, it will describe in details how to mitigate the risk associated with Nox. The mitigation will avoid any unwanted explosion. Which has occurred in several cold box of olefin plant across the globe. This paper will provide the safe & operational guide lines only for olefin plants. It should be carried out in each olefin plant to accesses the risk associated and mitigate as per the feed & impurities.

INTRODUCTION TO Nox chemistry:

The formation of Nox compound in cold box is due to presence of trace amount of Nox & oxygen in olefin feed. There are other several sources & contamination presence in cold box feed i.e. NH_3,RNH_2 etc. Which lead to formation of Nox gum & salt, when, it react with hydrocarbon at low temperature and high pressure. Numerous articles have been published about refinery gas stream. But our discussion is limited to olefin plant's feed contamination & other sources in petrochemical industry.

Other sources:

a. Chemical additive added in quench water & de-ethanizer are of amine functional group. It is being added to control the Ph & avoid polymer formation in pipeline.

b. Chemical additive added in caustic tower to avoid the gum formation or accumulation due to high storage capacity of spent caustic.
c. Saturated & non saturated gas streams.
d. Dilution steam
e. Make up water contamination in Boiler feed water additives.
f. Recycle streams.
g. Olefin feed contamination.
h. There are yet unidentified source of Nox contamination.

The chemistry of Nox accumulation is complex, though it has been explained as narrated below.

1. Low temperature reaction of Nox.
   2NO (nitric oxide) + O2 (oxygen)= 2 NO2 (nitrogen di- oxide)
   Note: Formation of NO2 favored by low temperature & high pressure. Conversion of NO expected to be highest at low temperature below -100 deg.C.
2. NO + NO2 = N2O3 (Di-nitrogen trioxide: A blue color liquid)
   Note: It is also favored by low temperature & high pressure . The reaction with any NO2 is virtually 100 %.
3. N2O3 (Di-nitrogen trioxide: A blue color liquid) can react
   a. with ammonia (NH3) at low temperature & high Pressure to form NH4Nox gums.

   (NO+O2) or N2O3+NH3 = NH3NO2 & NH3NO3 (ammonium nitrite & nitrate)

   b. With conjugated di-olefins to form Nox gums.

   N2O3 + Unsaturated hydrocarbon (e.g.1:3 Butadiene) = Nox gums

4. Physical properties of Nox:
   NO2 is highly acidic and is well removed by acid gas treatment. NO is not removed by conventional acid gas treatment. NO is approximately fractionated with methane.
   Both NO2 & N2O3 are solid at typical cold box temperatures. Solubility of NO2 & N2O3 in hydrocarbon is expected to be low. Therefore, NO2 or N2O3 can be freeze out & deposited in cold box. There are significant deposit of Nox gum & salt has been measured.

5. Nox hazards & toxicity:
   US threshold limit values (TLV)- Time weighted average for NO is 25PPM & for NO2 is 3PPM. On warming, N2 O3 = NO+NO2, If any one exposed for 60-minitues to 100PPM NO2 can lead to Pulmonary edema & death. It is reference from Patty's Industrial Hygiene & technology.

6. Nox gum & Salt accumulation Area.
   Low temperature zones of cold box favored the formation of NO2 & N2O3. There are certain area in cold box, where hydrocarbon get evaporated and leave solid & heavy hydrocarbons. Nox salts & gums are frequently found in coldest liquid section at about -165 deg.C feeding to de-methanizer.

7. NOx Gums
   NOx gum generally formed at lowest cold box temp. NOx gum stability depends on degree of nitration and accumulation at a given points(Agglomeration). Quick warming up of the cold box (e.g. as a result of process upset) is the most vulnerable time for explosion. NOx gums get unstable and even decompose explosively at temperature well below ambient.

8. NOx Salts

NOx salts generally formed at Temp below -100C. NOx salts decompose explosively at ambient temperature (NH4NO2) or at elevated temperature (NH4NO3). Explosive in nature similar to TNT. Explosion temp of NOx salts depend on size/shape of deposit and heat transfer characteristics.

Note: NOx gums are more dangerous than NOx salts since the decomposition starts at much lower temperatures.

9. Analysis of No and Nox Compounds:

Trace levels of No is very difficult to detect. The preferred method for measuring NO in cold box feed, is to use on line analyzer equipped with photo ionization detector(PID). Nox salt or gum recovered in alcohol washes

can be measured using the conventional anion & Cation ion chromatography.

BACKGROUD & OBJECTIVE:

Several incident and explosion has been reported due to Nox gum & salt accumulation in the cold box of olefin plant recovery section. It is important to recognize the Nox accumulation, can or has occurred and to take corrective steps to manage the risk associated with the possible or unknown accumulation. The current paper will described methodology of risk assessment on processing the steam cracked hydrocarbon products contaminated with Nox salts & gums in olefin plant of various type of feed and provide safety guide line to avoid potential accumulation in cold box.

Only small amount of Nox gums & salt is sufficient to cause an explosion with significant force to rapture the cold box tubes. But this question , yet to be answered.

METHODOLOGY OF RISK ASSESSMENT:

It has been advised to all the olefin plant to carry out the risk assessment of their own plant. There are olefin plant with different type of feeds and different technology suppliers. Risk assessment methodology was developed based on operating experience and knowledge shared by various agencies & licensors. The following criterion were used to assess the Risk level.

1. Pervious indication of Nox compounds.
2. Type of olefin feed & its contaminates.
3. Highest Pressure & Lowest temperature in Cold Box.
4. Additive and inhibitor containing the Nitrogenous compound.
5. Process of Recycle streams containing nitric oxides or nitrogen.
6. Amount of Naphtha & Heavies condensate in cold box.
7. Process Equipment Layout.
8. Possibility of di-olefin carry over during the process upset.
9. Is there possibility of impurities carry over by front end acetylene convertor

10. Is there possibility in the front end de-ethanizer, depropanizer to reduce risk of Nox impurities.

Risk Categories were defined as listed in Table-1.

No	Risk Level	Criteria
1.	Low	Ethane Feed: Possibility of contamination of feed with nitrogen cannot be ruled out. Moreover, feed was never being identified containing excessive amount of nitrogen, Nox etc. Limited number of additives are being dosed. Plant lay out (e.g. C2 front end hydrogenation, de-ethanizer etc.). Therefore, possibility of carry over the Nox or Nox derivates are least and formation of Nox gums & salts are almost negligible.
2.	Medium	Propane& Butane (C3&C4)Feed: Possibility of contamination of feed by Nox & nitrogen cannot be ruled out. Type of additives & inhibitors, high steam to HC ratio. Plant upset, Shutdown (S/D) and start up will increase the possibility of carry of di-olefins & heavies.
3.	High	Naphtha & Heavy Hydrocarbon Feed: Possibility of contamination of feed by Nox & nitrogen cannot be ruled out. Process of recycle streams, Many type of additives & inhibitors used. High steam to hydrocarbon ratio. Very low temperature in cold box. Plant upset, shutdown & start up will increase the possibility of carryover of di-olefin & heavies. Positive indication of Nox salts & gums were found during the methanol wash.

OPERATIONAL & SAFETY RECOMMENDATION:

1. ROUTINE SYSTEM MONITORING;
    a. Awareness of Nox, Nox gums & Salts formation.
    b. Online Nox analyzer to be installed at the inlet of cold box.
    c. Monitoring of temperature & pressure of cold process vessel & pipeline.
    d. Pressure drop across the cold services.
    e. Evaluation of heat transfer coefficient of cold exchangers.
    f. Establish procedure & practices to Flush drain legs on regular interval that normally operate below -80 deg.C.

g. Perform methanol wash at cold temperature as possible in every turnaround. Analyze for Nox gum & salts.
h. Establish components base materials balance across the cold box.
i. Report for any blue liquid and brown gases during the shutdown.

2. SHUTDOWN OF OLEFIN PLANT:
   a. Planned shutdown:
      1. Nitrogen is to be used to warm the cold box at control rate as per the recommendation of Fin-plate exchanger or cold box supplier.
      2. Drain liquid from warm drums to avoid any Nox gums & salts accumulation during the warming up.
      3. Monitored the expected rise in concentration of Nox as temperature rise up to -40 Deg.C.
   b. Unplanned shutdown:
      1. Loss of refrigeration or emergency shutdown: establish procedures to avoid butadiene or Nox gum & salts accumulation.

3. START UP OF OLEFIN PLANT.
   a. Planned start up: Cold box is to be cleaned by derimming prior to start up of plant. Nox salts & gums measurement is to be carried out during methanol wash.
   b. Unplanned start up followed by unplanned shutdown:
      i. Keep monitoring the Nox accumulated area. If necessary purge at control rate to flare without affecting the much variation in temperature & pressure. The most important aspect of unplanned shutdown & start up is not to allow the cold box to be warmed.
      ii. Carry out the immediate start up activity, If possible, isolate the cold box and carry out the proper purging prior to start up or line up again in the loop. It may lose the production but avoid explosion or incident.

iii. Stabilized the process stream & analysis for Nox & its impurities prior to line up.

4. UPSET IN OLEFIN PLANT: If any upset observed during the operation of the plant, then following is to be practiced.

a. Chilling train is to be blocked . This is to prevent heavy dienes moving forward to coldest section of the plant & form Nox gums.

b. Once chilling train blocked, monitored the temperature & pressure.

c. If temperature of the coldest section rise to -90 deg.C, then chilling train should be depressurized by venting from the inlet.

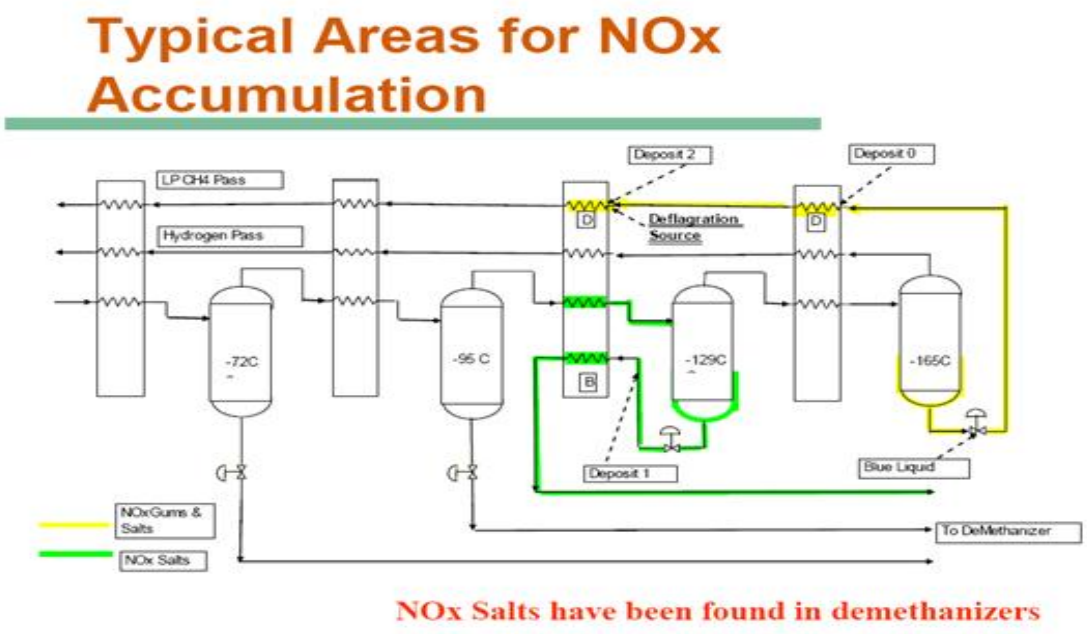
d. If pressure starts to drop due to valve passing, either leak is to be arrested or chilling train is to be depressurized from inlet.

e. If chilling section is to be restarted after shutdown, heavies materials should be excluded from chilling section until close to normal operating temperature are achieved.

f. Consider draining all the drums containing butadiene when forward flow is lost.

A SABIC APPROACH:

SABIC own & operate twelve (12) major olefin plants from various technology holder with various type of feeds. The capacity of their plants are varying from 800KTA to 1350 KTA. SABIC has conducted Risk assessment as per methodology mentioned above. Though, SABIC never had any incident due to Nox salts & gum formation or accumulation in cold box. All the olefin plants are categories under low, medium & high risk as described in above table. All the methodology are being practiced widely to avoid any unforeseen incident. Cold Box of each olefin plants are being operated as per feed at different temperature & pressure along with other operating conditions. Moreover, SABIC has identified the typical area of Nox salts & gums accumulation in Cold Box as illustrated in figure.



CONCLUSIONS:

Several forums are active to exchange information on accumulations of Nox salts & gums in the cold box. SABIC own and operate twelve (12) olefin plant with varieties of feed i.e. from ethane to heavy hydrocarbon . A methodology as described above , was developed to access the risk associated with Nox in various olefin plants of SABIC. Operation and safety recommendation was developed and being followed in each olefin plant. It has help us to avoid any unforeseen events so far. Therefore, it is suggested that each olefin plant may carry out the risk associated with Nox for their plant. If possible, follows suggested recommendation to avoid any unwanted incident.

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