AIChE Safety in Ammonia Plants
and Related Facilities Symposium
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Methanol Emission from Ammonia Plants and its Reduction

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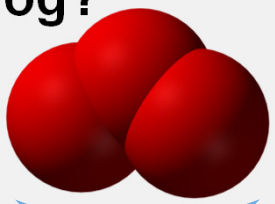
Methanol Emission from Ammonia Plants and its Reduction

- **Overview:**
  - Introduction:
    What is ozone smog?
  - Link to ammonia industry:
    Methanol emissions from ammonia plants are contributing to ozone smog
  - Solution:
    Reduction of methanol emission

Introduction
Ozone Smog

- **Summer Smog (also called Ozone Smog):**
  - Well-known phenomenon in many parts of the world
  - Affects our daily life:
    - attacks human health
    - restricts outdoor activities
- **What is ozone and ozone smog?**
  - Ozone molecule: O_3
  - Formed by:

air pollutants and oxygen (O_2)



under the influence of sunlight

Introduction
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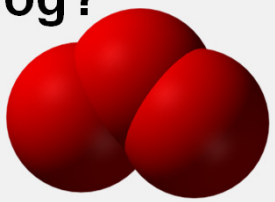


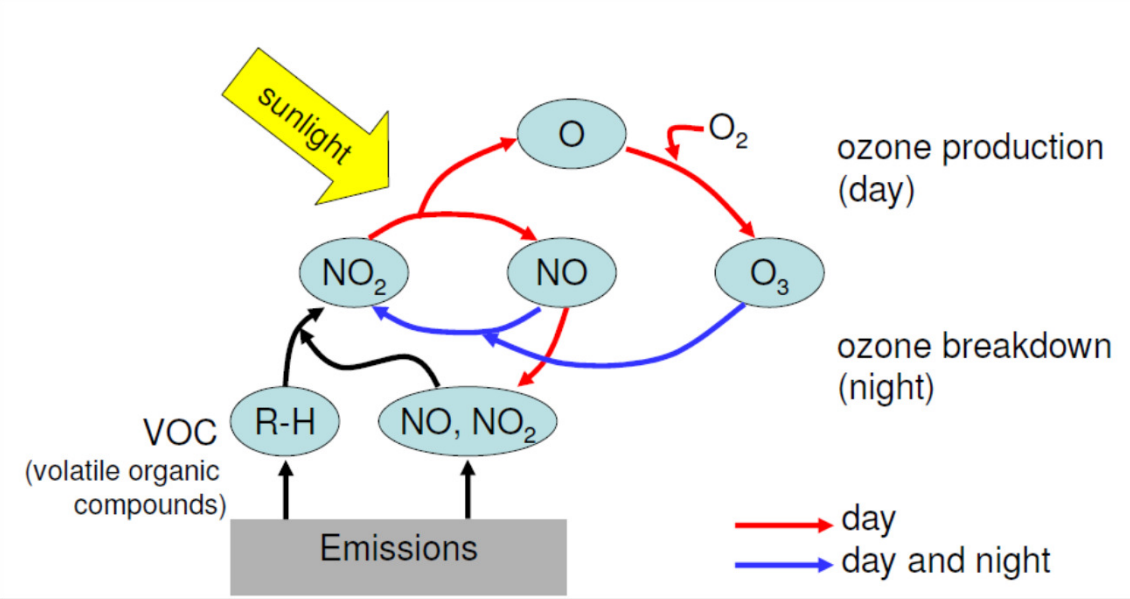
Note: Do not confuse **ozone smog** with the **ozone hole.**

- Ozone near ground (troposhere): attacks health
  ⇒ Avoid ozone formation!
- Ozone in stratosphere: protects against UV radiation
  ⇒ Protect the ozone layer!

Introduction
Ozone Smog

- **How is ozone smog formed?**

  Simplified mechanism:



  - Ozone formed from nitrous oxides (NO_2) in presence of UV radiation (sunlight)
  - Volatile organic compounds (VOC) are favouring this formation
  - VOCs from emissions from traffic and industry
  - Decomposition of ozone by reaction with NO

  Result: Equilibrium concentration of ozone in the atmosphere

Introduction
Ozone Smog

- **What are the effects of ozone smog?**

  Ozone enters the lungs, can cause inflammation. Possible effects:

  – coughing

  – irritation of the eyes

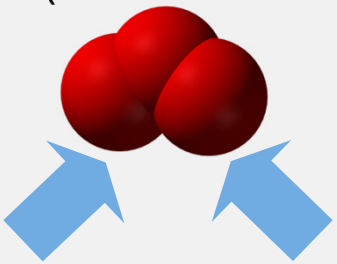
  – headache

  – functional disturbance of the lungs

  ⇒Avoid physical exercise when ozone levels are high

Introduction
Ozone Smog

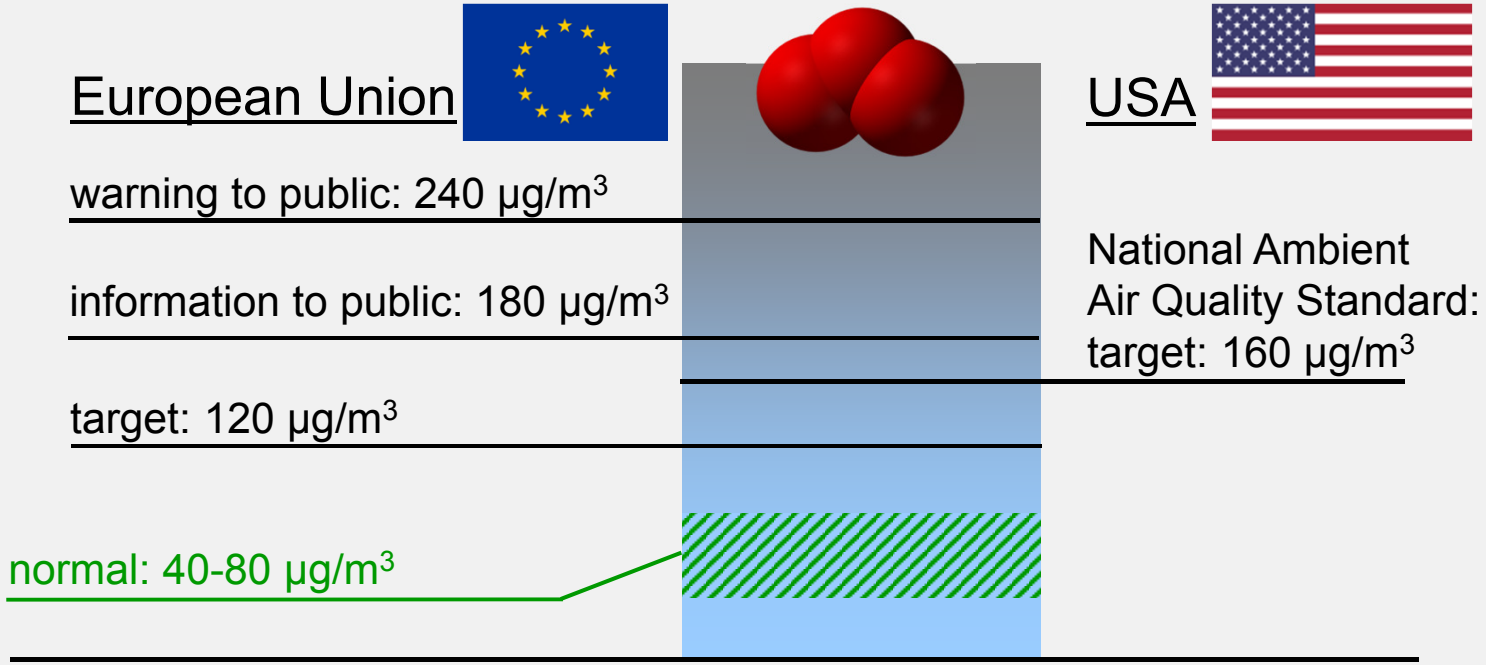
- **Ozone control (1):**
  - Ozone is not a direct emission – formed in the atmosphere, triggered by emissions (VOC and NO_x) and sunlight


  - Can only control emission of precursors – examples:
    - Catalyst for combustion engines: reduces NOx, CO and VOC (uncombusted fuel)
    - NOx removal systems for large furnaces:
      - ✓ fossil fuel power stations
      - ✓ industrial firings (also reformers in many places)

Introduction
Ozone Smog

- **Ozone control (2):**
  - Define limits to warn the population and to impose ban on certain emissions, e.g. by limiting traffic – examples:

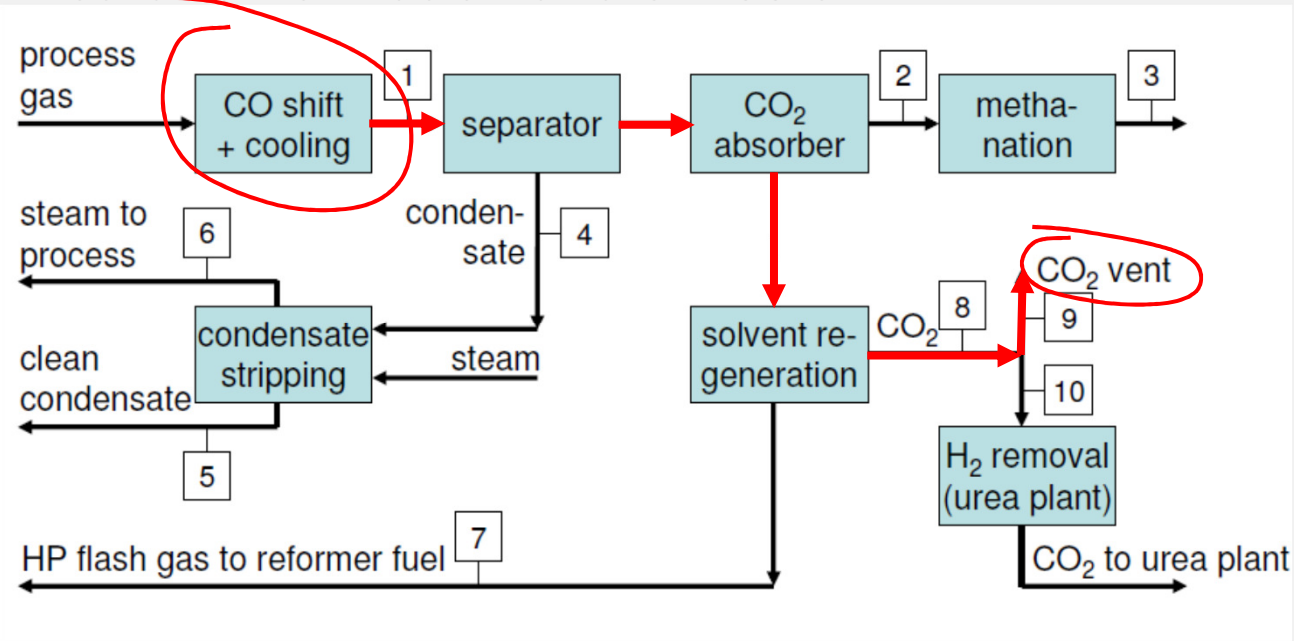


Methanol Formation in the Ammonia Plant
CO Shift

- **How does it affect the ammonia industry?**
  - Ammonia plants are emitting methanol, which is a VOC and is contributing to ground-level ozone formation
  - Where is methanol emitted?
  - Where is methanol formed?
  - How can we reduce formation and / or emission?

Methanol Formation in the Ammonia Plant
Overview

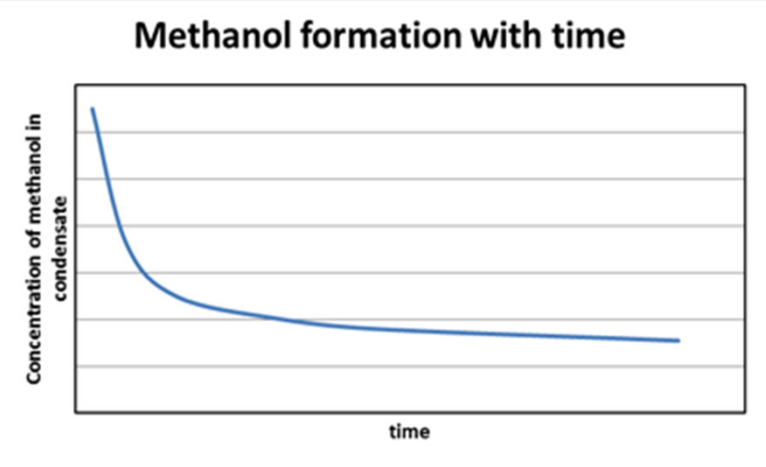
- **Methanol formation and emission**



  - Methanol CH_3-OH:
    - Formed as a by-product in HT and LT CO shift
    - Emitted from CO_2 removal unit together with CO_2

Methanol Formation in the Ammonia Plant
CO Shift

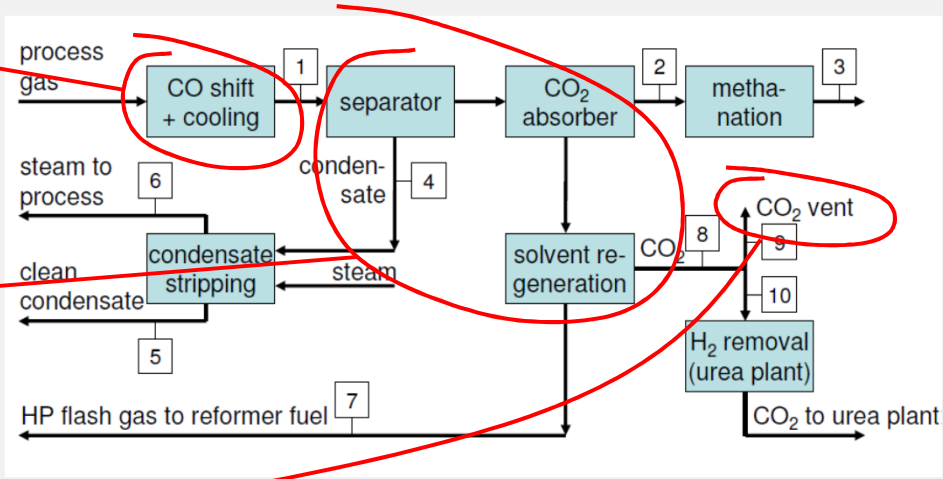
- **Methanol formation in CO shift:**
  - HT shift: small amount formed, limited by equilibrium
  - LT shift: potential for high formation, limited by kinetics
    - Activity with regard to methanol formation declines over time



    - No impact on activity with regard to CO shift reaction

Methanol Emission Reduction
Overview

- **Options for reducing methanol emissions:**
  - Reducing the amount formed
  - Removal or decomposition within the process
  - Removal or decomposition at the point of emission
  - Combination of the above schemes



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Methanol Emission Reduction

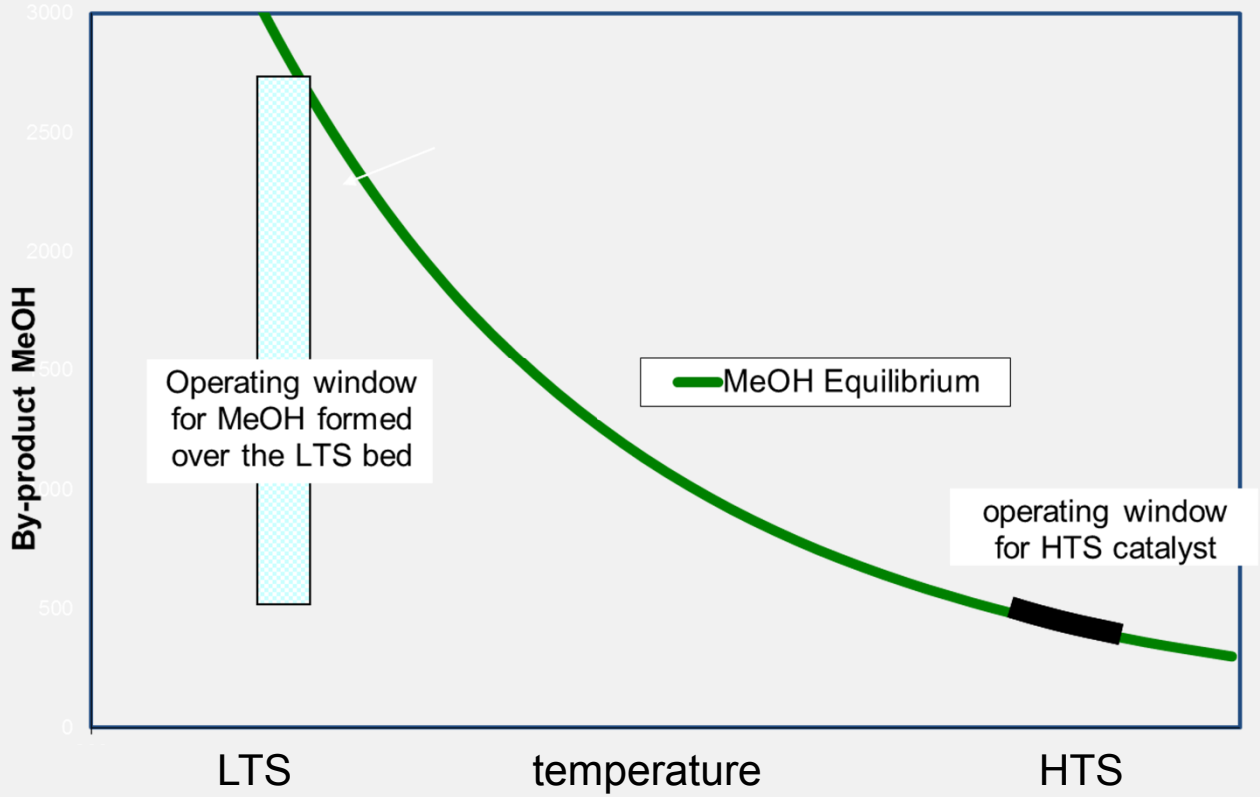
Reduction of Methanol Formation

- **Reducing methanol formation in LT shift catalyst:**
  - Change of process conditions:
    e.g. increase amount of steam, decrease pressure:
    - no very effective reduction
    - not much flexibility in conditions
  - Selection of catalyst type:
    - Selective low methanol LT shift catalysts such as KATALCO$_{JM}$ 83-3X: reduction of methanol formation by about 90% compared to conventional catalysts
    - Catalyst supplier can predict methanol formation from HT and LT shift

Methanol Emission Reduction

Reduction of Methanol Formation

By-product methanol as a function of temperature



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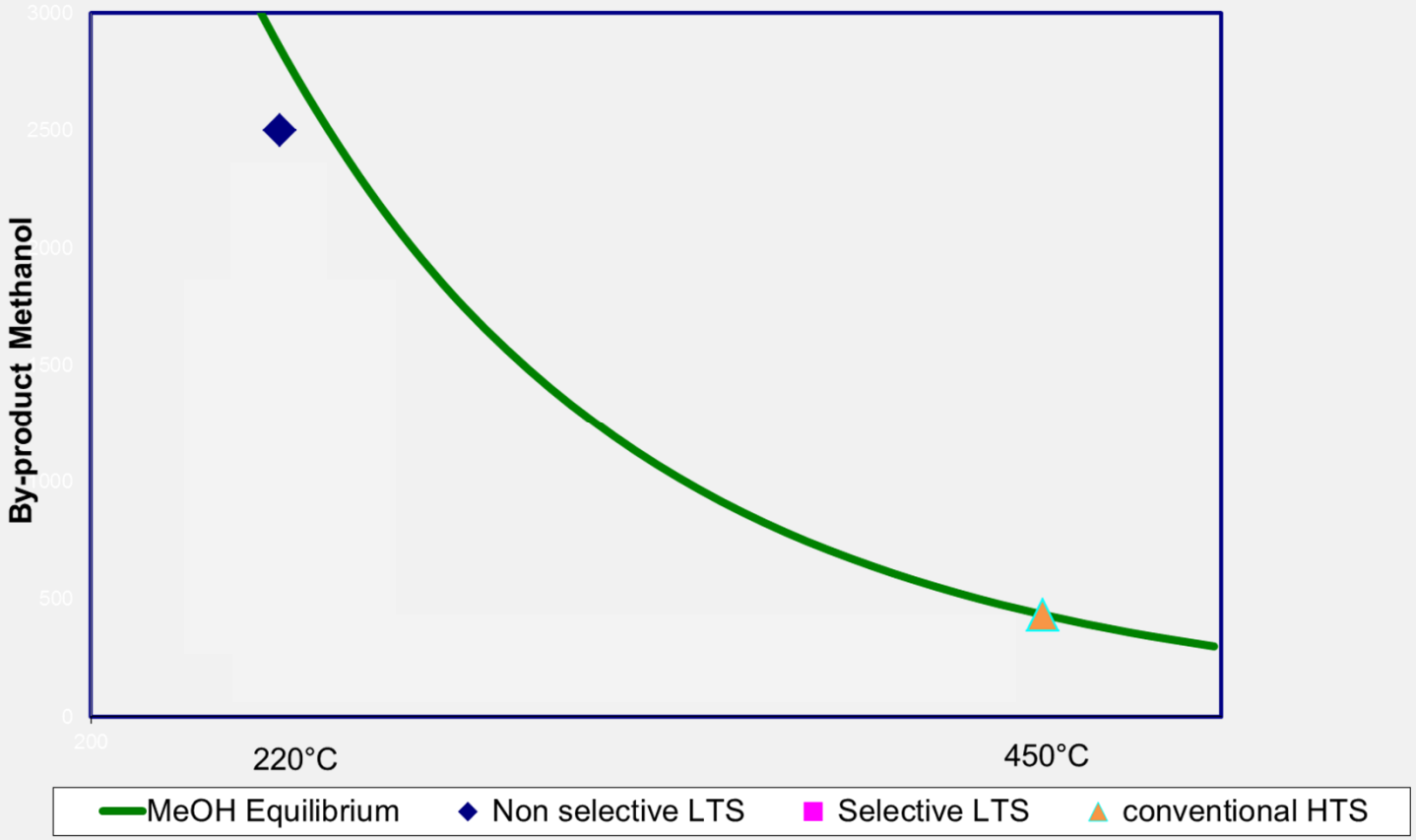
Methanol Emission Reduction

Reduction of Methanol Formation

By-product methanol from HTS and LTS catalysts



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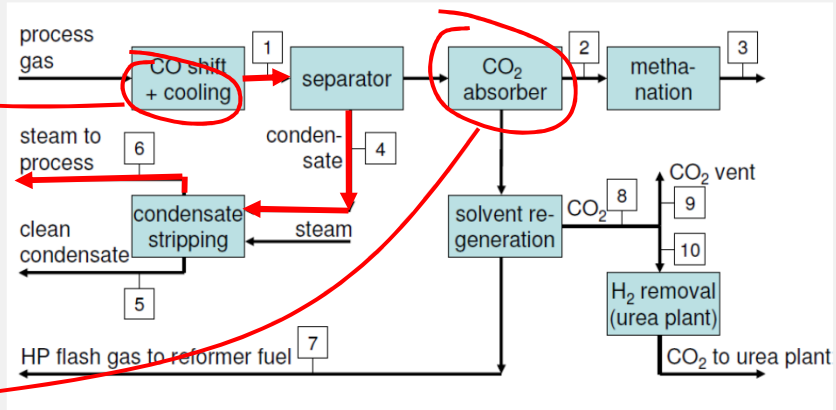
Methanol Emission Reduction

Reduction of Emission by Process Measures

- **Reduction of emission – divert methanol to process condensate:**
  - Typical process conditions:
    - Inlet temperature to amine-based absorber: ≈70 °C (≈160 °F)
    - 50 % or more of the methanol produced ends up in the process condensate
  - Effect of lower temperature:
    - More methanol to condensate, not ending up as emission
    - Higher load on cond. stripper
    - Requires taller absorber
  - Cooling by cooling water possible
  - Chilling by NH_3 as refrigerant: higher investment and operating cost



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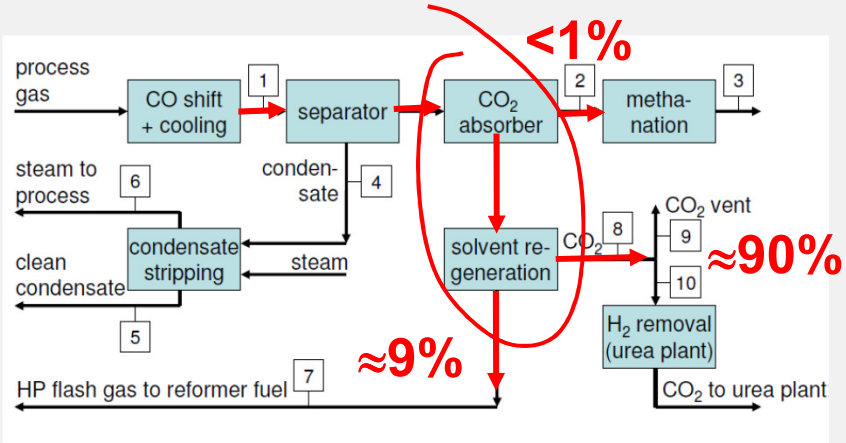
Methanol Emission Reduction

Reduction of Emission by Process Measures

- **Reduction of emission – changes in CO_2 removal system:**
  - Example:
    - two-cycle activated MDEA system, e.g. BASF OASE® white
    - typical distribution of the methanol entering CO_2 removal:



    - Hardly possible to influence the methanol balance by process variations like:
      no. of wash trays, pressure of intermediate flash etc.

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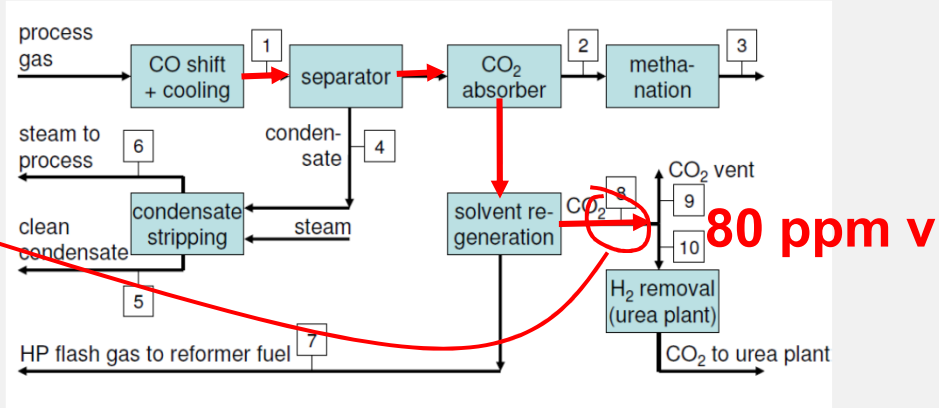
Methanol Emission Reduction

Removal at the Point of Emission of Emission

- **Removal at point of emission – absorption:**
  - Example:
    - trapping methanol in process condensate downstream CO_2 coolers
    - need make-up water
    - send methanol-rich stream to condensate stripper
    - lowest methanol level that can be achieved at CO_2 vent:
      - ✓ with normal temperatures: ≈80 ppm v
      - ✓ reduction only by ≈20 ppm v when using lower temperature of 10 °C (50 °F)



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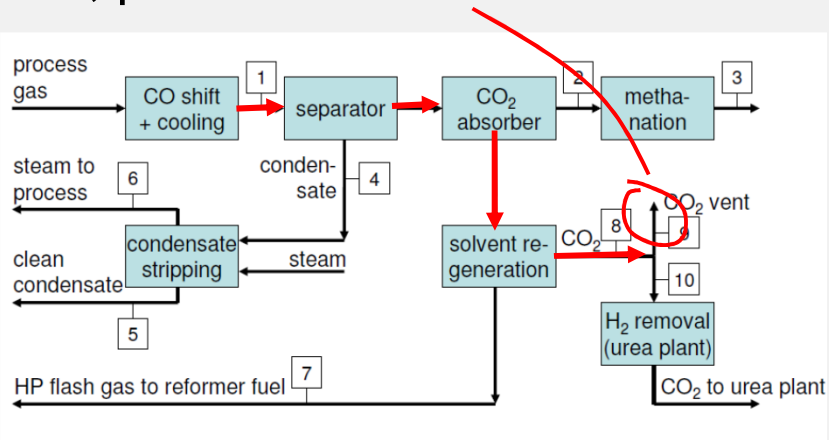
Methanol Emission Reduction

Removal at the Point of Emission of Emission

- **Removal at point of emission – destruction by catalytic oxidation:**
  - Using technology for VOC removal, proven in other industries
  - Requires slight excess of oxygen



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Methanol Emission Reduction

Removal at the Point of Emission of Emission

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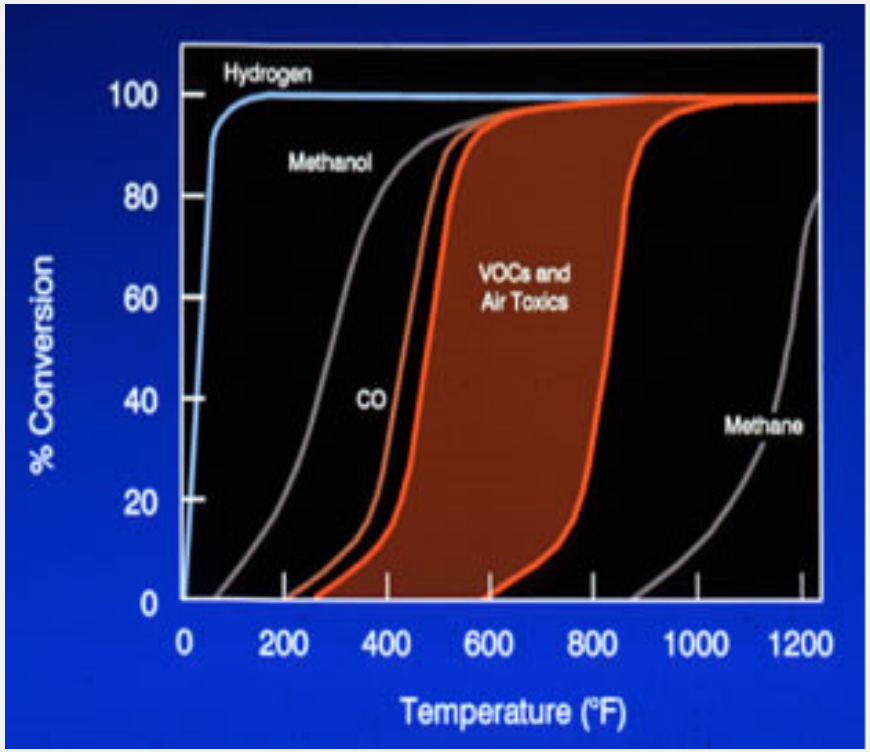
  - Using technology for VOC removal, proven in other industries
  - Requires slight excess of oxygen
  - High temperature needed for full conversion

$$CH_3OH + 1\tfrac{1}{2}\ O_2 \rightarrow CO_2 + 2\ H_2O$$



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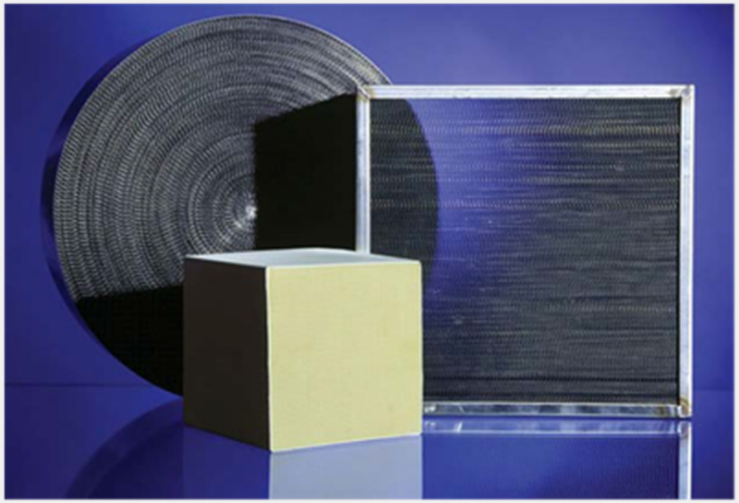
Methanol Emission Reduction

Removal at the Point of Emission of Emission

- **Removal at point of emission – destruction by catalytic oxidation:**
  - Using technology for VOC removal, proven in other industries
  - Requires slight excess of oxygen
  - High temperature needed for full conversion
  - Result: few ppm methanol
  - Catalyst types:
    - ✓ Monolithic catalysts coated with thin layer of platinum or palladium to minimize pressure drop
    - ✓ When the CO_2 is at pressure, catalyst pellets more economic



Summary

- Methanol emissions from ammonia plants are considered to contribute to ground-level ozone (same as other VOC emissions).
- Targets and regulations exist to reduce VOC emissions
- Regulators are starting to pay more attention to VOC emissions on ammonia plants and this trend is likely to increase.
- Technical options to reduce these emissions:
  - Reducing methanol by-product formation in the LTS catalyst
  - Modifying the CO_2 removal process
  - End-of-pipe solution
- Lowest VOC emissions can be achieved only by catalytic conversion at the point of emission. – By combination with the above options, amount of methanol to be converted in the emission stream can be lowered.

Thank you
for your attention!

Questions?

Comments?

Suggestions?

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