VOC, HAP and Odor Control Options for Industry and Manufacturing

A&WMA FALL CONFERENCE
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What’s the VOC Problem?
Generation of ground level ozone via reaction with NOx

- Lots of names: VOCs, HAPs, NCG's, nuisance odors
- Multiple regulations: HAPS, SOCMI-HON, PHARMA
- Examples:
  - Solvent emissions from coating and mixing
  - Gasoline and diesel fumes from tanker truck loading
  - High concentration fumes from chemical processes
  - NCG's (noncondensable gases) from processes
  - Refinery tanks and petroleum terminals
  - Sludge remediation projects and tank cleanouts
Basic Design Data

• Process flowrate and temperature of VOC stream
• Concentration of the VOCs
• Composition of carrier
  – Nitrogen, Oxygen, Air, Steam/Water Vapor
• Chemical properties (especially Cl, S)
• Particulates, ash, soot, silicon dust
• Nature of process (continuous, cyclical, variable flow and VOC composition)
• Potential application for use of waste heat
• State and federal regulations
Optimizing abatement system choice

The wrong choice means higher fuel use and emissions!
Control Options - Collection with Activated Carbon

- Must prevent ignition due to heat of absorption!
  - Need sprinklers
  - Need CO/CO2 detectors/thermocouples to detect ignition
  - Must be below dewpoint entering carbon
- Zeolites also used -- similar to carbon
- Membranes also used for polyolefins and other VOCs
- Desorb/condense for recovery, or concentrate for oxidizer, or ship carbon offsite for disposal/regeneration
Refrigerated Condensers

• Used for high concentrations (e.g., 500,000 ppm/50% by volume organics) and low flows
• Allows recycle of organics from single source processes, e.g., gasoline transfer operations
• Condensation from multisource processes can yield a mixture of organics which is not useable and has low market value
Limits of Flammability vs. Inert Percent in Air

% Air = 100% - % Combustible Vapor - % Inert

COMBUSTIBLE VAPOR, volume percent

UEL

LEL

T<sub>1</sub>

T<sub>2</sub> > T<sub>1</sub>

INERT, volume percent

Non-flammable mixtures

Flammable Mixtures
## LEL/UEL of Pure Gases and Vapors in Air

**Rule-of-Thumb -- 25ºF Rise per 1% LEL**

<table>
<thead>
<tr>
<th>Gas or Vapor</th>
<th>Lower Limit % Vol</th>
<th>Upper Limit % Vol</th>
<th>Gas or Vapor</th>
<th>Lower Limit % Vol</th>
<th>Upper Limit % Vol</th>
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<tbody>
<tr>
<td>Acetaldehyde</td>
<td>4.0</td>
<td>57</td>
<td>Butyl cellosolve</td>
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<tr>
<td>Acetone</td>
<td>2.5</td>
<td>12.8</td>
<td>Carbon disulfide</td>
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<tr>
<td>Acetylene</td>
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<td>80</td>
<td>Carbon monoxide</td>
<td>12.5</td>
<td>74.2</td>
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<tr>
<td>Allyl alcohol</td>
<td>2.5</td>
<td>--</td>
<td>Chlorobenzene</td>
<td>1.3</td>
<td>7.1</td>
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<tr>
<td>Ammonia</td>
<td>15.5</td>
<td>26.6</td>
<td>Cottonseed oil</td>
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<td>--</td>
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<tr>
<td>Amyl acetate</td>
<td>1.0</td>
<td>7.5</td>
<td>Cresol, M- or p-</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Amylene</td>
<td>1.6</td>
<td>7.7</td>
<td>Crotonaldehyde</td>
<td>2.1</td>
<td>15.5</td>
</tr>
<tr>
<td>Benzene (benzol)</td>
<td>1.3</td>
<td>6.8</td>
<td>Cyclohexane</td>
<td>1.3</td>
<td>8.4</td>
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<tr>
<td>Benzyl chloride</td>
<td>1.1</td>
<td>--</td>
<td>Cyclohexanone</td>
<td>1.1</td>
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</tr>
<tr>
<td>Butene</td>
<td>1.8</td>
<td>8.4</td>
<td>Cyclopropane</td>
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<td>10.5</td>
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<tr>
<td>Butyl acetate</td>
<td>1.4</td>
<td>15</td>
<td>Cymene</td>
<td>0.7</td>
<td>--</td>
</tr>
<tr>
<td>Butyl aclohol</td>
<td>1.7</td>
<td>--</td>
<td>Dichlorobenzene</td>
<td>2.2</td>
<td>9.2</td>
</tr>
</tbody>
</table>
Direct Fired Thermal Oxidizers

• Refractory lined chamber + burner
• Fouling not an issue with correct design/layout
• For odor control, 1200°F is minimum
• General guidelines:
  – 90% destruction of VOCs, operation @1450-1500°F minimum, dependent upon VOC
  – 98% DE, 1600°F @ 0.75 sec. residence time
  – Halogenated VOCs, 1800°F @ minimum 1 sec. with high intensity burner/good mixing
  – With low intensity flame burner, 2 sec. minimum res. time
• For recuperative type, add HX to preheat VOC stream:
  – Plate type < 1400°F; shell & tube type > 1400°F
Direct Thermal Oxidizer

Upfired – with no acid gas or dust

Rich/Lean “DeNOxidizer for fuel bound N2
Used with permission Callidus
Steps Required for Successful Oxidation of Dilute Fumes

1. Mixing of Fume and Hot Combustion Gases
2. Retention of Fumes at High Temperature for Sufficient Time
3. Clean Effluent

- Supplemental Fuel
- Outside Air (If Used)
- Dilute Fume

Fume to Supply Oxygen for Fuel Combustion (Outside Air Needed If Fume Fouls Burner or is <16% Oxygen)
Fluid Dynamics – Mixing of waste Gas and Flame

Baffles frequently used, e.g., “disk and donut,” to provide macro mixing
OXIDIZER WITH HEAT RECUPERATOR

WASTE GAS
10000 SCFM
200° F

Oxidizer

1600° F

Heat Recuperation

850° F

Stack

NATURAL GAS 1500 SCFH
PLUS 8 MM Btu/hr VOC
Shell and Tube Heatexchangers – Tube Side

Bellows for Expansion
Plate Type Heat Exchanger

- Exhaust air stream exits the exchanger.
- Supply air stream enters at opposite end, in a counterflow manner.
- Supply air stream exits, enhanced with recovered energy.
- Hot exhaust air stream enters the exchanger.
Catalytic Oxidizers

- For low concentrations, typically, 5-15% LEL
- Provides good oxidation at reduced temp
- Frequently use HX to preheat fume stream, typically to 600°F
- Usual max temp 1200°F
- Fouling/poisoning an issue (platinum deactivated by chlorinated compounds) with lead, arsenic and phosphorous
- Particulate can blind catalyst pores
- Catalysts for chlorinated VOCs (Chromia alumina, cobalt oxide, copper/MgO)
- Periodic catalyst replacement required
HX can be added to make it catalytic-recuperative, preheating the fume.
RTO (Regenerative Thermal Oxidizer)

- Used for 3-5% LEL VOCs; W/hot gas bypass, up to 20-25% LEL
- Very high (95%) energy recovery, 5% of fuel required for direct flame oxidizer
- High capital cost, very low operating cost
- Uses a “heat sink” of heat absorbing ceramic materials
- Two chamber units have trouble achieving high (e.g., >98%) DE
- Best to use 3 chamber or puff chamber types to reduce momentary low DE during valve change over for odor control and higher DE
- Circular/rotary valve type has internal purge, similar to 3 chamber/puff chamber type
RTO (Regenerative Thermal Oxidizer) Critical Design Issues

- **Cold face build up** (if organic, use auto bakeout cycle)
- **Fog/mist** entering beds, best to use coalescing mist eliminator upstream, and two or three chamber with bakeout
- **Condensate** in the underbed plenums, increase cycle time/raise exhaust/underbed plenum to keep plenums dry
- **Dust plugging** the beds (need filter upstream)
- **Corrosion**: Wall temp is cool and SO2/HCl may reach dewpoint; use mastic coat on walls or SS alloy
RTO Cutaway View

- Independent Burners
- Clean Process Air
- Purge Air
- Heat Exchange Media
- Solvent-Laden Process Air

Used with permission Durr Environmental
Three Bed RTO With Bed Purge for Off-Cycle Bed

Used with permission Durr Environmental
VOC Controls -- Flares

• For waste gases above LEL
• Steam injection or air assist for “smokeless” flare
• Elevated flare minimizes radiation to ground and surrounding structures
• Ground flare conceals flame in refractory lined chamber
• For process upsets, rapid pressure rise or rapid production of VOCs or more constant flow/small vents that are not recoverable for useful heat (e.g., LFG)
• Per EPA AP-42 and 40 CFR 65.147, the following minimum fuel values are required for elevated flares:
  – Steam-assisted - 300 Btu/scf
  – Air-assisted - 300 Btu/scf
  – Non-assisted - 200 Btu/scf
  – Can boost with natural gas to achieve minimums
  – 98% Destruction efficiency assumed
Elevated Flare Tip
Elevated Flare
Shielded Elevated Flare

Used with permission of John Zink Company
VOC System Safety and Explosion Issues
NFPA Codes Re Ignition in VOC Systems

- Most oxidizers operate < 25% LEL, which is NFPA 86 Limit for combustion equipment with standard controls
- NFPA 86 allows up to 50% LEL with extra controls: “where a continuous solvent indicator and controller is provided” ... plus “alarm and shut down” to “not exceed 50 percent of the LEL”
- Engineered systems operate above 50% LEL, e.g., flares, with proper protection, such as seal pots, and proper design and operation
- Controls must be able to monitor all the combustibles that may enter the oxidizer; problems may occur, e.g., with vapor analyzers that don’t see fuel value of liquid droplets
Flame Arrestors Used for Some Applications

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Georgia Case Study – Blue Haze Abatement

- Application: Pine veneer drying
- VOCs, terpenes, blue haze = submicron droplets
- Design flow and VOC data suspect: Tuned burners, got a higher true value at 30,000 acfm and VOCs
- Chose 2 chamber RTO with auto-programmed bakeout cycle to address cold face buildup
- Preliminary design of ducts, all sloped to drip tee
- Wrote spec, got quotes, helped client negotiate contract
- Supplied permit and compliance input
Georgia Case Study – Coating Operation RTO

- Two chamber RTO to control spray paint solvent VOCs
- Troubleshooting for:
  - Low VOC destruction efficiency on stack test
  - Recycle vs. exhaust volume not right at spray booths
- Findings:
  - Several thousandths gap on 3’ diameter switching valves causing bypassing of raw VOC and low DRE
  - Open emergency vent on roof allowed outside air in, plus air leakage into system at filter bank upstream of RTO both lowering exhaust volume from booths
Questions?

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