September 23, 2016

MEMORANDUM

To: Alison Eyth and Madeleine Strum, OAQPS, EPA

From: Greg Yarwood and, Tejas Shah, Ramboll Environ, Novato, CA

Subject: Composition of organic gas emissions from flaring

Summary

Ramboll Environ analysed data on the composition of organic gas emissions from an air-assisted flare and developed chemical speciation profiles for total organic gas (TOG) emissions for flaring natural gas. The resulting speciation profiles are based on measured data and should be preferred over SPECIATE profile 0051 (Flares - Natural Gas) which is based on engineering judgement. The methodology presented here can be used to develop application-specific flare speciation profiles that account for the composition of the vent gas being flared.

The formaldehyde content of flare emissions is of specific interest because formaldehyde is photo-chemically reactive and a hazardous air pollutant (HAP). For the natural gas flaring profiles developed here, the formaldehyde/VOC ratios range from 5.3% to 12.6% whereas the formaldehyde/TOG ratios range from 1.2% to 3.9%. For comparison, SPECIATE profile 0051 (Flares - Natural Gas) has 40% formaldehyde/VOC and 20% formaldehyde/TOG.

Background

Flares are used to abate venting of natural gas and other combustible gases for safety reasons and to reduce the environmental impacts of venting hydrocarbons. When a flare is operated within design criteria the destruction and removal efficiency (DRE) of the vented gas can be very high, approaching 100%. Nevertheless, small amounts of un-combusted vent gas will escape the flare combustion zone and, in addition, products of incomplete combustion will escape the flare combustion zone.

Speciation profiles are needed to apportion TOG emissions from flaring to individual organic gases. Flares in-service at natural gas producing facilities have been observed operating at very high DRE (Caulton et al, 2014) and lesser DRE (Strosher, 2000) depending upon vented gas composition and operating conditions. It would be useful to have speciation profiles that are appropriate for different ranges of DRE performance.

SPECIATE profile 0051 is used for natural gas flaring but was developed in the 1980s using engineering judgment (Sonnichsen, 1980). There is a need to replace profile 0051 with speciation profiles for natural gas flaring that are based on data. The objective of this work was to develop TOG speciation profiles for natural gas flaring.

In 2010, the Texas Commission on Environmental Quality (TCEQ) sponsored a flare study that was conducted by The University of Texas at Austin (UT) at the John Zink test facility in Tulsa, OK (Torres et al., 2012; Allen and Torres, 2011). The TCEQ flare study provides comprehensive and detailed emissions composition data for two flares operated over ranges of conditions and vent gas composition. However, the TCEQ flare study was designed to understand emissions from industrial flares used in petrochemicals manufacturing and does not directly provide speciation profiles that are applicable to natural gas flaring. Nevertheless, the TCEQ flare study is the best available source of information on composition of flare TOG emissions.

The TCEQ flare study provides data on TOG speciation from steam assisted and air assisted flares (Torres et al., 2012). Torres et al. (2012) summarize the TCEQ flare study methods and results as follows:

“A series of full-scale industrial flare tests were conducted at low flow and low BTU content of flared gases at an industrial test facility. Both a 24” diameter air-assisted flare with a flow capacity of 144,000 lb/h and a 36” steam-assisted flare with a flow capacity of 937,000 lb/h were employed in the testing. Flared gases were mixtures of natural gas, propylene, and nitrogen or natural gas, propane, and nitrogen. Natural gas to propane or propylene ratio was 1:4 by volume for all experiments. Nitrogen was used as a diluent to achieve the desired lower heating values (LHV) for the vent gas. The range of flared gas flow rates was 0.1% to 0.65% of the flare’s design capacity. Flare operation was characterized by measurements of flow rates to the flare, extractive measurements made of the vent gases fed to the flare, extractive measurements made at the end of the flare plume, and remote sensing measurements of the flare plume made by a variety of spectroscopic instruments. Destruction/removal efficiencies (DRE, fraction of vent gas reacted) of flared species were calculated based on the observed composition of the species in the plume. The tests demonstrated that destruction efficiencies for steam-assisted flares drop dramatically when combustion zone heating values fall below 250 BTU/scf. Air-assisted flares showed a linear drop in DRE as a function of air flow. While the primary focus of the measurements was on DRE, products of incomplete combustion were also measured. Dominant products of incomplete combustion were CO, ethylene, formaldehyde, acetylene, and acetaldehyde. CO represented approximately 24% to 80% (carbon basis) of the total products of incomplete combustion for DRE > 90%. While DREs of 98–99% were observed in some experiments, many operating conditions produced DREs of substantially less than 99%. Since prescribed methods for estimating emissions would have predicted 98–99% DRE for all the tests, some test conditions resulted in the production of flare emissions multiple times the value that would be calculated using the prescribed estimation methods. In practice, total emissions from flares will depend on both operating conditions and the duration of operation at the various operating conditions.”

Steam or air assistance to industrial flares promotes rapid mixing of the vent gas with ambient air to improve combustion efficiency and mitigate smoke formation. Flares used in oil and natural gas production may be unassisted or air assisted (e.g., <http://www.aereon.com/flare-systems>) but are unlikely to be steam assisted because steam would not be readily available. We analyse data for the air assisted flare as being more representative of flares used in oil and natural gas production. Strengths of the TCEQ flare study are comprehensive speciation of the vent gas and the combustion products in the flare plumes. Limitations of the TCEQ flare study (for addressing our objective) are that the type of flare and the fuel used are not matched to oil and natural gas production.

Analysis of TCEQ Flare Study Results

Organic gas composition found in the plume of an air assisted flare burning a propylene/natural gas mixture is presented in Table 1. Allen and Torres (2011) report these data as mass per mass of propylene which we convert to weight percent of TOG. The organic gas weight percent data from Table 1 are plotted against DRE in Figure 1 by assigning a representative DRE value to each reported DRE range (e.g., DRE < 0.8 is plotted as DRE of 0.7). The compounds plotted in Figure 1 can be classified as unburned vent gas (propylene, methane, ethane) or products of incomplete combustion (the other gases) and this classification can explain variations in weight percent with DRE. Weight percentages of unburned vent gases rise as DRE falls whereas weight percentages of most combustion products fall with lower DRE (butane isomers are an exception, discussed below). These trends are consistent with more vent gas escaping the combustion zone at lower DRE and diluting the weight percentages of combustion products (butenes are an exception, discussed below).

The products of incomplete combustion identified in Table 1 can be explained by chemical reactions known to occur in hydrocarbon combustion (e.g., Ranzi et al., 2012). Ethylene and acetylene are ubiquitous products of hydrocarbon pyrolysis formed by cracking fuel molecules and by radical reactions in fuel-rich portions of the flame. Small aldehydes (formaldehyde, acetaldehyde) are ubiquitous products of hydrocarbon oxidation formed in portions of the flame that contain oxygen. Combustion products containing 3 carbon atoms (acetone, propanal, propylene oxide) are likely to be from propylene which also has 3 carbon atoms. Butenes show a different dependence on DRE than other combustion products in Figure 1 suggesting that they are formed by a unique mechanism such as interaction between propylene from the vent gas and carbene radical (CH2) formed by combustion.

By assuming that products of incomplete combustion in Table 1 containing 1 or 2 carbon atoms are ubiquitous in hydrocarbon flames we derive representative composition for products of incomplete combustion shown in Table 2. The composition data in Table 2 are unsuitable for directly speciating flare emissions because they contain no unburned vent gases.

By summing weight percentages of unburned vent gases and products of incomplete combustion from Table 1 we obtain relative contributions of these two species categories to total TOG emissions from a flare shown in Table 3.

Speciation Profiles for Flaring Natural Gas

The relative contributions of unburned vent gas and products of incomplete combustion shown in Table 3 provide a basis for developing complete flare speciation profiles. The products of incomplete combustion can be speciated using data from Table 2 whereas the unburned vent gas can be speciated using application-specific data such as the produced-gas composition for a particular natural gas play. This method is illustrated using data from SPECIATE profile # 8949 "Natural Gas Production" shown in Table 4. The TOG speciation profiles for flaring natural gas shown in Table 5 are composited from the speciation data in Tables 2 and 4 using relative contributions in Table 3. The profiles in Table 5 can be used as default speciation for flaring natural gas if the composition of the vented natural gas is unknown.

The formaldehyde content of flare emissions is of specific interest because formaldehyde is photo-chemically reactive and a HAP. The formaldehyde/VOC ratios for the profiles shown in Table 5 range from 5.3% to 12.6% whereas the formaldehyde/TOG ratios range from 1.2% to 3.9%. For comparison, SPECIATE profile 0051 (Flares - Natural Gas) has 40% formaldehyde/VOC and 20% formaldehyde/TOG.

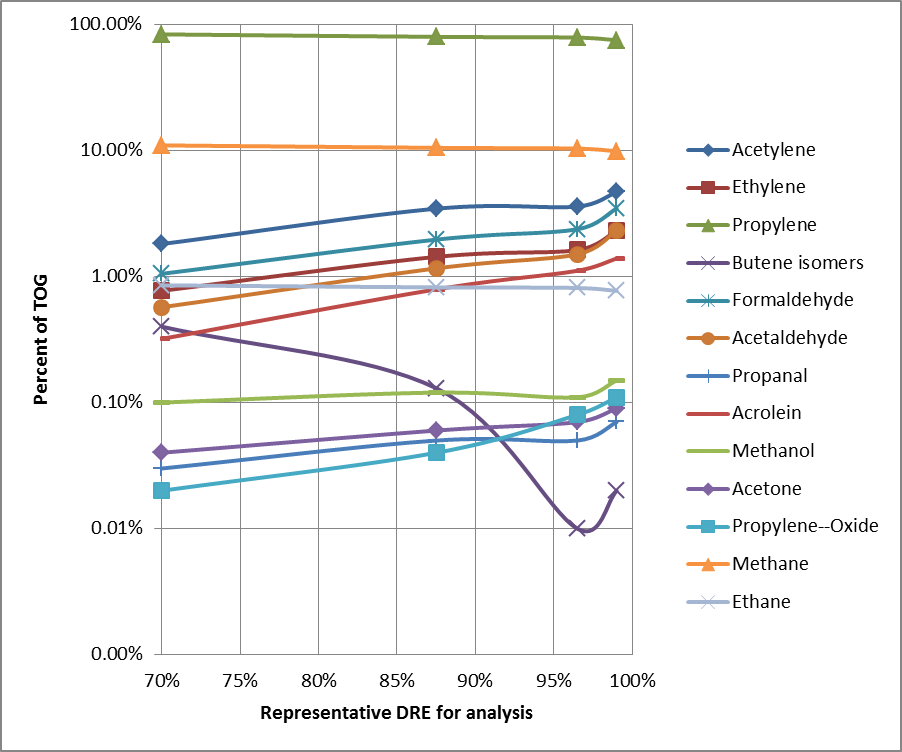


Figure 1. Organic gas composition found in the plume of an air assisted flare burning a mixture of 80% propylene and 20% natural gas (Allen and Torres, 2011).

Table 1. Organic gas composition found in the plume of an air assisted flare burning a mixture of 80% propylene and 20% natural gas. Data were reported by Allen and Torres (2011) as mass per mass of propylene and converted here to weight percent of TOG.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Compound** | **Mass per mass of Propylene** | | | | **Weight percent of TOG** | | | |
| **DRE Range** | | | | **DRE Range** | | | |
| **> 0.98** | **0.95 to 0.98** | **0.8 to 0.95** | **< 0.8** | **> 0.98** | **0.95 to 0.98** | **0.8 to 0.95** | **< 0.8** |
| **Vent Gas Constituents** | | | | | | | | |
| Propylene | 1 | 1 | 1 | 1 | 74.80 | 78.35 | 79.50 | 83.08 |
| Methane | 0.1318 | 0.1318 | 0.1318 | 0.1318 | 9.86 | 10.33 | 10.48 | 10.95 |
| Ethane | 0.0103 | 0.0103 | 0.0103 | 0.0103 | 0.77 | 0.81 | 0.82 | 0.85 |
| **Products of Incomplete Combustion** | | | | | | | | |
| Acetylene | 0.0625 | 0.0457 | 0.0433 | 0.0218 | 4.68 | 3.58 | 3.45 | 1.81 |
| Ethylene | 0.0307 | 0.0207 | 0.018 | 0.0093 | 2.30 | 1.62 | 1.43 | 0.77 |
| Butene isomers | 0.0002 | 0.0002 | 0.0017 | 0.0048 | 0.02 | 0.01 | 0.13 | 0.40 |
| Formaldehyde | 0.0463 | 0.0303 | 0.0247 | 0.0127 | 3.46 | 2.37 | 1.96 | 1.05 |
| Acetaldehyde | 0.0308 | 0.0192 | 0.0146 | 0.0069 | 2.30 | 1.50 | 1.16 | 0.57 |
| Propanal | 0.001 | 0.0007 | 0.0007 | 0.0004 | 0.07 | 0.05 | 0.05 | 0.03 |
| Acrolein | 0.0186 | 0.0142 | 0.0099 | 0.0038 | 1.39 | 1.11 | 0.79 | 0.32 |
| Methanol | 0.002 | 0.0014 | 0.0016 | 0.0012 | 0.15 | 0.11 | 0.12 | 0.10 |
| Acetone | 0.0012 | 0.0008 | 0.0008 | 0.0005 | 0.09 | 0.07 | 0.06 | 0.04 |
| Propylene oxide | 0.0014 | 0.001 | 0.0006 | 0.0002 | 0.11 | 0.08 | 0.04 | 0.02 |
| Total | -- | -- | -- | -- | 100% | 100% | 100% | 100% |

Table 2. Composition for products of incomplete combustion for use in developing flare speciation profiles.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Compound** | **DRE Range** | | | |
| **> 0.98** | **0.95 to 0.98** | **0.8 to 0.95** | **< 0.8** |
| Formaldehyde | 27% | 26% | 24% | 24% |
| Methanol | 1% | 1% | 1% | 2% |
| Acetaldehyde | 18% | 16% | 14% | 13% |
| Acetylene | 36% | 39% | 42% | 42% |
| Ethylene | 18% | 18% | 18% | 18% |
| Total | 100% | 100% | 100% | 100% |

Table 3. Relative contributions of unburned vent gas and products of incomplete combustion for use in developing flare speciation profiles.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Component of Flare Emissions** | **DRE Range** | | | |
| **> 0.98** | **0.95 to 0.98** | **0.8 to 0.95** | **< 0.8** |
| Unburned vent gas | 85% | 89% | 91% | 95% |
| Products of incomplete combustion | 15% | 11% | 9% | 5% |
| Total | 100% | 100% | 100% | 100% |

Table 4. SPECIATE profile # 8949 "Natural Gas Production"

|  |  |
| --- | --- |
| **Compound** | **Weight Fraction** |
| Methane | 6.95E-01 |
| Ethane | 1.12E-01 |
| Propane | 8.56E-02 |
| Butane | 5.71E-02 |
| Pentane | 2.85E-02 |
| Hexane | 4.12E-03 |
| Benzene | 8.78E-04 |
| Toluene | 7.82E-04 |
| 2,2,4-trimethylpentane | 1.16E-03 |
| Ethylbenzene | 4.97E-05 |
| Isomers of xylene | 2.22E-04 |
| Isomers of hexane | 1.48E-02 |

Table 5. Default TOG speciation profiles for flaring natural gas.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Compound** | **Compound SPECIATE ID** | **DRE Range** | | | |
| **> 0.98** | **0.95 to 0.98** | **0.8 to 0.95** | **< 0.8** |
| **Weight Fraction** | | | |
| Formaldehyde | 465 | 3.91E-02 | 2.71E-02 | 2.22E-02 | 1.25E-02 |
| Methanol | 531 | 1.69E-03 | 1.26E-03 | 1.36E-03 | 1.19E-03 |
| Acetaldehyde | 279 | 2.60E-02 | 1.72E-02 | 1.32E-02 | 6.78E-03 |
| Acetylene | 282 | 5.29E-02 | 4.10E-02 | 3.91E-02 | 2.15E-02 |
| Ethylene | 452 | 2.60E-02 | 1.86E-02 | 1.62E-02 | 9.16E-03 |
| Methane | 529 | 5.93E-01 | 6.22E-01 | 6.31E-01 | 6.59E-01 |
| Ethane | 438 | 9.57E-02 | 1.00E-01 | 1.02E-01 | 1.06E-01 |
| Propane | 671 | 7.32E-02 | 7.66E-02 | 7.77E-02 | 8.13E-02 |
| Butane | 592 | 4.88E-02 | 5.11E-02 | 5.18E-02 | 5.42E-02 |
| Pentane | 605 | 2.44E-02 | 2.55E-02 | 2.59E-02 | 2.71E-02 |
| Hexane | 601 | 3.52E-03 | 3.69E-03 | 3.74E-03 | 3.91E-03 |
| Benzene | 302 | 7.50E-04 | 7.85E-04 | 7.97E-04 | 8.33E-04 |
| Toluene | 717 | 6.68E-04 | 7.00E-04 | 7.10E-04 | 7.42E-04 |
| 2,2,4-trimethylpentane | 118 | 9.94E-04 | 1.04E-03 | 1.06E-03 | 1.10E-03 |
| Ethylbenzene | 449 | 4.25E-05 | 4.45E-05 | 4.51E-05 | 4.71E-05 |
| Isomers of xylene | 507 | 1.90E-04 | 1.99E-04 | 2.02E-04 | 2.11E-04 |
| Isomers of hexane | 2127 | 1.26E-02 | 1.32E-02 | 1.34E-02 | 1.40E-02 |

Table 6. Ratios of formaldehyde, VOC and TOG for natural gas flaring profiles.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Ratio** | **DRE Range** | | | |
| **> 0.98** | **0.95 to 0.98** | **0.8 to 0.95** | **< 0.8** |
| Formaldehyde/TOG | 3.9% | 2.7% | 2.2% | 1.2% |
| Formaldehyde/VOC | 12.6% | 9.8% | 8.3% | 5.3% |
| VOC/TOG | 31% | 28% | 27% | 23% |

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