Vehicle Refueling Emissions

Refueling Emission Inventories and Regulatory Policy

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Overview

• What are vehicle refueling emissions?
• What hydrocarbon compounds are in refueling emissions?
• Why should we care about refueling emissions?
• What factors affect the per vehicle refueling emission rate?

• Case 1: USA
• Case 2: China
• Case 3: EU
• Case 4: Brazil
What are vehicle refueling emissions?

- VOC vapor and entrained droplets displaced from the fuel tank ullage.
- Any fuel spilled during the refueling event.

Mostly of concern for volatile liquid fuels (>2 psi RVP)
VOC Composition of Refueling Emissions

- Refueling vapors are dominated by (C4 and C5) compounds (butanes and pentanes); liquid gasoline is dominated by a variety of heavier (C6 to C9) compounds.

- Addition of ethanol changes vapor composition but it remains dominated by lighter weight compounds (C5 or less).

SAE Paper 880712: “Factors Influencing the Composition and Quantity of Passenger Car Refueling Emissions - Part II”
Why Control Refueling Emissions? – O₃ Reactivity

- Ozone is formed through photochemical interactions of VOCs and NOx. Many different VOCs are emitted into the atmosphere, each reacting at different rates and with different reaction mechanisms.
- The differences in rates of ozone formation are referred to as the ozone "reactivity" of the VOCs and are quantified through Reactivity Adjustment Factors (RAFs).
- Ozone RAFs have been determined for each VOC.
- The lighter weight compounds which are dominant in gasoline vapor are moderately reactive. However, they represent such a large fraction of the total emission mass, that reducing lighter ends through RVP control is a major ozone reduction strategy.
- In this sample, C4-C5 compounds represent 65% of ozone forming potential emissions from gasoline vapor.
- VOCs, such as aromatic compounds, also form secondary organic aerosols (PM₂.₅). The fraction of aromatic compounds varies with gasoline grade.

* SAE Paper 860086: “Composition of Vapor Emitted from a Vehicle Gasoline Tank During Refueling”
** 17 CCR 94700: “Maximum Incremental Reactivity Values for Compounds - 2010”

<table>
<thead>
<tr>
<th>Compound</th>
<th>liquid*</th>
<th>mass %</th>
<th>CA ARB</th>
<th>mass vapor</th>
<th>mass %</th>
<th>mass %</th>
<th>RAF**</th>
<th>wtd RAF</th>
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<td>propane</td>
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<td>0.49</td>
<td>0.65%</td>
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<td>n-butane</td>
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<td>1.21</td>
<td>3.1</td>
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<td>n-hexane</td>
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<td>isobutane</td>
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<td>isopentane</td>
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<td>methylcyclopentane</td>
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<td>2-methyl-1-butene</td>
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<td>0.5</td>
<td>6.4</td>
<td>2.24%</td>
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<td>cis-2-butene</td>
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<td>0.5</td>
<td>14.24</td>
<td>4.98%</td>
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<td>trans-2-butene</td>
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<td>0.5</td>
<td>15.16</td>
<td>5.30%</td>
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<tr>
<td>cis-2-pentene</td>
<td>0.21</td>
<td>0.5</td>
<td>10.38</td>
<td>3.63%</td>
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<td>toluene</td>
<td>18.01</td>
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<td>4</td>
<td>6.44%</td>
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<tr>
<td>benzene</td>
<td>2.9</td>
<td>1.5</td>
<td>0.72</td>
<td>0.76%</td>
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</tbody>
</table>
Air Toxic Exposures

• Gasoline vapor contains compounds which adversely affect health

• Occupational health impacts for service station attendants:
  • At higher concentrations, gasoline vapor may result in adverse impacts
    • **Symptoms:** irritant, dermatitis, headache, lassitude, blurred vision, dizziness, slurred speech, confusion, convulsions; chemical pneumonitis; possible liver, kidney damage
  • ACGIH 8-hr gasoline vapor TLV is 300 ppm and the 15-min.; STEL is 500 ppm.
  • Even at very low concentrations, benzene vapor may result in adverse impacts
    • Hematotoxicity and potential carcinogen (leukemia)
    • ACGIH 8-hr benzene TLV is 0.50 ppm and the 15-min. STEL is 2.5 ppm.

• Community health impacts
  • No identified chronic exposure standards for gasoline vapor or benzene, only AEGLs.

Refueling VOC Emission Rates

• Between 1972 and 1988 there were at least six studies which evaluated uncontrolled refueling emission rates on a g/gal basis.

• Each study gave a slightly different results depending on the vehicles evaluated and the range of the key experimental factors included such as the vapor pressure and temperatures.

• A 1988 study by the CRC (VE-6) was the most comprehensive. The relationship in the equation below reflects a fill from 10% to 100%. It is the equation used by EPA.

\[
g/gal = \exp[-1.2798 - 0.0049(\Delta T) + 0.0203(T_d) + 0.1315(RVP)]
\]

• Where \( \Delta T = (T_{tank} - T_{dispensed}) \); temperatures are in °F, RVP is in psi
Factors Affecting the VOC Emission Rate

• Three primary factors:
  • Reid vapor pressure (RVP) of fuels
  • Dispensed fuel temperature $T_d$
  • Tank fuel temperature $T_t$
• Several secondary factors:
  • Dispensing rate
  • Tank and fillpipe configuration
  • Initial volume of fuel in tank and volume dispensed
• Ethanol/methanol blends affect RVP. RVP control is needed.

Benzene Refueling Emission Rate

Largely dependent on volume % benzene in liquid fuel. (mass % = 0.85 vol %)

\[ Bz \text{ (g/gal)} = 0.052 \text{ (vol\% Bz liquid)} \]

Observations

- Based on headspace equilibrium measurements, 1% benzene in liquid yields 0.43% in vapor or 4300 ppmv.
- At STP, this converts to 13737 mg/m\(^3\) or about 0.05 g benzene/gallon.
- Limited data from vehicle testing suggests that benzene emission rate is also affected by any entrained droplets and vapor shrinkage or growth.*


Spillage

- Spillage is generally divided into four categories.
  - Pre-fill nozzle handling by the operator
  - Pre-mature shut-off spit back
  - End of fill event well back and topping off
  - Post-fill nozzle handling by the operator

- 1 ml spilled gasoline is about 0.7 g of VOC. Even a “drop” is about 0.05 g of VOC.

For conventional nozzles:
- EPA’s AP-42 (Chapter 5) estimates spillage at about 0.32 g/gallon dispensed
- ARB estimates 0.28 g/ gallon dispensed.*
  - For EVR Stage II and conventional nozzles, ARB has nozzle standards to reduce spillage.**
- API estimates 0.14 g/gallon dispensed.***

- Benzene mass in spilled fuel depends on benzene mass in liquid gasoline.
Technology for Refueling Emission Control

**Stage II Vapor Recovery Technology:** 70-75% efficiency

Refueling vapors are captured at the vehicle fillpipe outlet using a specially designed fuel nozzle and forced into underground storage tank. In balance-type systems, this returned vapor decreases fuel evaporation in the UST. During fuel delivery, if Stage I control is present, the tank vapors are routed back to the tanker truck as fuel is dropped. Stage II efficiency heavily dependent on user maintenance, inspections, and testing, as well as government oversight.

**ORVR Technology – 98% efficiency**

Refueling vapors are blocked from escaping through the fill pipe and instead captured on the vehicle’s activated carbon canister. The canister is purged during vehicle driving, and the vapor is burned as fuel. ORVR technology is integrated with vehicle’s current evaporative control system hardware. ORVR designs also reduce spillage during refueling. ORVR is applicable to all types of gasoline-powered highway vehicles.
Case Evaluations
Case 1: The US (mature fuel and technology control programs)

US VOC Refueling Emission Inventory

US Benzene Refueling Emission Inventory
Case 2: China (benzene control and ORVR for 2020)

China has Stage II in several major cities, but the implementation rate and efficiency are unknown.
Case 3: EU 28 member states (widespread Stage II, but still phasing-in)

Brazil (uses gasoline C blend (E25) and E100 fuel)
Six Areas Refueling Emission Inventory Trends

Vehicle Refueling VOC Emissions

Vehicle Benzene Refueling Inventories
Conclusions

• Refueling emissions are significant sources of VOCs and air toxics
  • Control provides reductions in ozone, SoA (PM$_{2.5}$), and air toxics
  • Inventories depend directly on gasoline and gasoline-blend consumption
    • Trends are definitely for reduced use of volatile fuels based on improved fuel economy requirements and powertrain electrification

• There are well established control techniques available.
  • Vehicle control: 98% efficient
  • Stage II: 70-75%
  • Fuel quality: RVP limits, benzene limits and use of oxygenate and gasoline-oxygenate blends

• Analysis indicates significant inventory implications for Brazil and India which have no controls and project fuel large demand increase.
Thank you for your kind attention.

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Vapor Generation During Refueling

A Study Of Variables that Effect The Amount of Vapor Emitted During the Refueling of Automobiles, E.M. Liston, SRI, May 1975.
Benzene concentration in refueling vapor varies with fuel benzene content (mass % = 0.85 vol %)

\[
\text{vol}\% \text{ Bz vapor} = 0.43 \times (\text{vol}\% \text{ Bz liquid})
\]

Vehicle Benzene Refueling Inventories

[Graph showing the trend of benzene inventories by region from 2020 to 2040. The x-axis represents calendar years 2020 to 2040, and the y-axis represents metric tons. Lines indicate inventories for the US, Japan, EU, India, China, Brazil with ORVR, and Brazil.]
Time-series Comparison of Refueling VOC Emission Inventories – 6 areas
Benzene refueling emission rate is impacted by dispensed ($T_d$) and fuel tank temperature ($T_t$).

Benzene Refueling Emissions: % vol vs. $T_d$; $\Delta T = 0$

Benzene Refueling Emissions: % vol vs. $\Delta T$ where $\Delta T = (T_t - T_d)$; $T_d = 70^\circ F$

$$Bz (g/gal) = 0.038(\% Bzm) - (1.60 \times 10^{-4} \times T_d) - (4.24 \times 10^{-4} \times \Delta T):$$ Equation from: SAE Paper 861559: Factors Influencing Benzene Emissions from Passenger Cart Refueling, October 1986.