

**Organic Gas Speciation Profiles for  
Running Exhaust of CNG (Compressed Natural Gas) Transit Buses  
Equipped with TWC (Three-Way Catalysts) — OG2403 & OG2404**

Wenli Yang, PhD, PE

Air Quality Planning and Science Division

10/16/2014

## **1. Introduction**

Two organic gas speciation profiles (OG2403 and OG2404) for compressed natural gas (CNG) transit buses equipped with three-way catalysts (TWC) were developed in this work to complement the current CARB organic gas speciation profile database. The profiles were created based on chassis dynamometer test data of two transit buses equipped with TWCs running on CNG. Profile OG2403 was made for Steady-State (SS) cruise cycle and Profile OG2404 was for Urban Dynamometer Driving Schedule (UDDS) cycle.

## **2. Methodology**

The emissions of methane, gaseous toxic hydrocarbons, carbonyls and polycyclic aromatic hydrocarbons (PAHs) from two CNG transit buses with stoichiometric 2007 Cummins ISLG 280 engine and TWC were measured in 2010 using the West Virginia University Transportable Heavy Duty Vehicle Emissions laboratory chassis dynamometer and the Transportable Emissions Measurement System set up at CARB's Stockton laboratory [1, 2].

The buses were tested over a high speed SS cruise driving cycle and a UDDS cycle. Samples for gaseous toxic compounds (including 1,3-butadiene, benzene, ethylbenzene, toluene, m,p-xylene, o-xylene, styrene) were collected in Summa canisters and analyzed by using a GC [3]. Carbonyl samples were collected from the dilution tunnels on 2,4-dinitrophenylhydrazine (DNPH) impregnated cartridges, extracted with acetonitrile and analyzed using a HPLC with an ultraviolet detector [4]. Vapor phase PAH samples were collected on pre-cleaned PUF/XAD cartridges placed downstream of the filters, extracted using dichloromethane and analyzed on a GC-MS [1]. However, except for the toxics and PAHs listed above, the speciation of other non-methane hydrocarbons (NMHCs) is not reported (or characterized) in these studies [1, 2]. In order to fill up the missing part of the unidentified NMHCs in the speciation profiles, three assumptions are made to estimate the emissions of the NMHCs as follows: (1) Methane is 98% of the THC, which is the average value obtained from several NG-TWC exhaust studies [5, 6]. This ratio is used to calculate NMHCs in this work; (2) The NMHCs mainly consist of gaseous toxic compounds (listed above), gaseous PAHs and light-end hydrocarbons [7]; (3) The composition of the light-end hydrocarbons in the CNG-TWC exhaust is similar to the one for the CNB buses without any after-treatment.

### 3. Results

The details of the speciation profiles are provided in Table 1. The ratios of TOG/THC (total organic gas/total hydrocarbon) are 0.997 for OG2403 and 0.998 for OG2404 assuming the molecular weight of TOG is 16.04 (the same as methane). The ratios can be used to convert THC emission mass to actual TOG weight. Based on the speciation profiles, the ROG/TOG ratios are 0.0162 and 0.0140 for OG2403 and OG2404, respectively.

In both profiles, methane is the predominant species. Table 1 indicates that 98% of the TOG emitted from CNG-TWC buses is methane; while carbonyl compounds and NMHCs are only 2%. Compared to the profiles for CNG buses without after-treatment (82% methane in OG2401 & OG2402), the methane content in the exhaust from TWC control system is greatly increased. On the contrary, the contents of aldehydes are significantly reduced in the profiles for CNG-TWC buses. Especially for formaldehyde, the weight percentage is about 10% in OG2401 and OG2402, and it drops to only 0.004% in OG2403 and O2404. Additionally, the NMHCs in OG2403 and OG2404 are also reduced. For example, among the seven target toxic compounds in OG2401 and OG2402, only benzene remains above the detection limit and shows up in OG 2403 and OG2404. These reductions are believed to be due to the high exhaust temperature from stoichiometric combustions, which increases the catalyst temperature and results in the high oxidation efficiency for aldehydes and NMHCs [1].

**Table 1. OG Speciation profiles for CNG-TWC buses**

<i>Species Name</i>	<i>SAROAD</i>	<i>Weight Percentage, %</i>	
		<i>OG2403 CNG-TWC Buses (SS)</i>	<i>OG2404 CNG-TWC Buses (UDDS)</i>
1-butene	43213	0.004670	0.005178
1-methylnaphthalene	91124	0.034294	0.021317
1-pentene	43224	0.000970	
2,6-dimethylnaphthalene	98185	0.021813	0.016932
2-methylnaphthalene	91123	0.063846	0.041384
acenaphthene	97002	0.006970	
acetaldehyde	43503	0.002936	0.002313
acetone	43551	0.007965	0.007204
acetylene	43206	0.040027	0.046209
benzene	45201	0.003399	0.002598
butyraldehyde	43510	0.000881	0.000816
cis-1,trans-2,3-trimethylcyclopentane	91038	0.001689	0.006623
ethane	43202	0.386318	0.604060
ethylene	43203	0.964279	0.952021
fluoranthene	97013	0.006970	
fluorene	97003	0.011406	
formaldehyde	43502	0.004410	0.004374
isobutane	43214	0.003275	0.011552
isobutylene	43215	0.001213	0.002227
isopentane	98132	0.003275	0.005790
methane	43201	97.983694	97.984134
methyl ethyl ketone (mek) (2-butanone)	43552	0.000095	0.000394
m-tolualdehyde	45502	0.000190	0.000787
naphthalene	98046	0.259031	0.081504
n-butane	43212	0.004003	0.011636
n-pentane	43220	0.000788	0.002060
phenanthrene	97005	0.065247	0.020712
propane	43204	0.039481	0.086851
propionaldehyde	43504	0.000450	0.000319
propylene	43205	0.076415	0.081005
<i>Total</i>		<i>100.000000</i>	<i>100.000000</i>

## References:

1. Yoon, S.; Hu, S.; Kado, N. Y.; Thiruvengadam, A.; Collins, J. F.; Gautam, M.; Herner, J. D.; Ayala, A., Chemical and toxicological properties of emissions from CNG transit buses equipped with three-way catalysts compared to lean-burn engines and oxidation catalyst technologies. *Atmospheric Environment* **2014**, *48*, 220-228.
2. Thiruvengadam, A.; Besch, M. C.; Yoon, S.; Collins, J.; Kappanna, H.; Carder, D. K.; Ayala, A.; Herner, J.; Gautam, M., Characterization of Particulate Matter Emissions from a Current Technology Natural Gas Engine. *Environmental Science & Technology* **2014**, *48*, (14), 8235-8242.
3. CARB, Procedure for the Determination of C2 to C12 Hydrocarbons in Automotive Exhaust Samples by Gas Chromatography: SOP MLD (Ver 2.2). In El Monte, CA, 2007.
4. CARB, Standard Operating Procedure for the Determination of Aldehyde and Ketone Compounds in Automotive Source Samples by High Performance Liquid Chromatography: SOP MLD 104. In El Monte, CA, 2006.
5. CARB, *EMFAC 2014 Documentation*. 2014.
6. Yoon, S.; Collins, J.; Thiruvengadam, A.; Gautam, M.; Herner, J.; Ayala, A., Criteria pollutant and greenhouse gas emissions from CNG transit buses equipped with three-way catalysts compared to lean-burn engines and oxidation catalyst technologies. *Journal of the Air & Waste Management Association* **2013**, *63*, (8), 926-933.
7. Ayala, A.; Gebel, M. E.; Okamoto, R. A.; Rieger, P. L.; Kado, N. Y.; Cotter, C.; Verma, N., Oxidation Catalyst Effect on CNG Transit Bus Emissions. *SAE Technical Papers* **2003**, 2003-01-1900