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Health assessment of gasoline and fuel oxygenate vapors: Generation and characterization of test materials

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ABSTRACT

In compliance with the Clean Air Act regulations for fuel and fuel additive registration, the petroleum industry, additive manufacturers, and oxygenate manufacturers have conducted comparative toxicology testing on evaporative emissions of gasoline alone and gasoline containing fuel oxygenates. To mimic real world exposures, a generation method was developed that produced test material similar in composition to the re-fueling vapor from an automotive fuel tank at near maximum in-use temperatures. Gasoline vapor was generated by a single-step distillation from a 1000-gallon glass-lined kettle wherein approximately 15–23% of the starting material was slowly vaporized, separated, condensed and recovered as test article. This fraction was termed vapor condensate (VC) and was prepared for each of the seven test materials, namely: baseline gasoline alone (BGVC), or gasoline plus an ether (G/MTBE, G/ETBE, G/TAME, or G/DIPE), or gasoline plus an alcohol (G/EtOH or G/TBA). The VC test articles were used for the inhalation toxicology studies described in the accompanying series of papers in this journal. These studies included evaluations of subchronic toxicity, neurotoxicity, immunotoxicity, genotoxicity, reproductive and developmental toxicity. Results of these studies will be used for comparative risk assessments of gasoline and gasoline/oxygenate blends by the US Environmental Protection Agency.

1. Introduction

In 1994, the Environmental Protection Agency (EPA) issued a final rule under the Clean Air Act (CAA) which adds new health effects information and testing requirements to the Agency's existing registration program for motor vehicle fuels and fuel additives (Registration of Fuels, 2013: § 79.56; Clean Air Act, 2012). The rule, referred to as the "211(b)" rule, required additional actions that must be taken to register or maintain product registration. Under the new registration program, producers of current and new motor vehicle fuel and fuel additives are required to provide information and test results to EPA regarding the composition of emissions from their products and the potential effects of these emissions on the public health and welfare. These new data requirements supplemented the existing registration requirements.

To help fulfill the new 211(b) requirements for gasoline and diesel fuel, the American Petroleum Institute organized the 211(b) Research Group ("Research Group"). The Research Group is an unincorporated group of over two hundred fuel, oxygenate, and fuel additive manufacturers affiliated by contractual obligation to meet the Tier 1 and Tier 2 testing requirements of Section 211(b)(2) and 211(e) of the Clean Air Act.

The Research Group's purpose was to address two of the three categories of fuel outlined in the 211(b) rule (40 CFR 79.56). Membership in the Research Group is open to any company which has an interest in the registration of these products with EPA. The Research Group tested; (1) "baseline" fuel groups which contain no elements other than carbon, hydrogen, oxygen, nitrogen and sulfur, and for gasoline contain less than 1.5% oxygen by weight, and for diesel contain less than 1.0% oxygen, and (2) "non-baseline" fuel groups which contain only the elements listed above but are either derived from nonconventional sources of oil, or contain in excess of 1.5% or 1.0% oxygen by weight for gasoline and diesel respectively. Oxygenates in non-baseline fuel groups tested by the Research Group were; ethanol (EtOH), tertiary-butyl alcohol (TBA), methyl tertiary-butyl ether (MTBE), ethyl tertiary-butyl ether (ETBE), tertiary-amyl methyl ether (TAME) and di-isopropyl

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ether (DIPE). The Research Group's testing scope does not include a third category of fuel groups, namely atypical fuel groups, which consist of fuels or fuel additives that contain elements other than carbon, hydrogen, oxygen, nitrogen and sulfur.

The toxicology studies required under Alternative Tier 2 of the 211(b) Rule are based on inhalation exposure to the evaporative emissions from baseline gasoline or oxygenated gasolines. The health endpoints included assessments for subchronic toxicity, neurotoxicity, genotoxicity, immunotoxicity, developmental toxicity, reproductive toxicity, and chronic toxicity/carcinogenicity. The results of chronic toxicity testing of gasoline and gasoline combined with MTBE have already been reported (Benson et al., 2011) and reported elsewhere in this issue are the findings for subchronic toxicity testing (Clark et al., 2014), genotoxicity (Schreiner et al., 2014), neurotoxicity (O'Callaghan et al., 2014), immunotoxicity (White et al., 2014), reproductive toxicity (Gray et al., 2014), and developmental toxicity testing in mice and rats (Roberts et al., 2014a, 2014b).

Generation of the evaporative emissions described in the original 211b rule at CFR 79.57(f)(2) required the construction of an "evaporative emissions generator (EEG)". The EEG was to be filled no more than 40% full with the fuel to be tested. The EEG was to be heated to 130 °F and the generated vapor was to be well mixed and used for inhalation exposures. The size and number of EEGs were to be varied to adjust the chamber atmosphere concentrations. No more than 7% of the fuel volume was to be lost during vapor generation and the fuel in the EEG was to be replaced at the end of each day. Those original rule requirements imposed significant logistical and safety issues for the toxicology testing facilities and the Research Group. Because of those issues, the Research Group undertook development of an alternative method for generating the evaporative emissions. The alternative method developed to generate and characterize the test articles used in the toxicology studies are reported in this paper.

2. Methods and materials

The gasoline (e.g., baseline gasoline) used to generate all the test articles is patterned after the reformulated gasoline summer baseline fuel as specified in CAA section 211(k)(10)(B)(i) (40 CFR 79.55). The specifications and blending tolerances for that gasoline are listed in Table 1 as well as the actual values for the first lot of baseline gasoline blended.

The additive types included in the CAA baseline gasoline specifications and the actual treat rates used for this testing program are also listed in Table 1. The test articles used in the inhalation toxicity studies are vapor condensates prepared from baseline gasoline and baseline gasoline plus oxygenate blends using the method described below. The method used to generate the vapor condensate test articles was developed at Chevron Energy Technology Company (Richmond, CA). Generation of the test articles was done using commonly accepted petroleum engineering practices.

2.1. Baseline gasoline and oxygenate blending

Baseline gasoline meeting CAA requirements was blended by Phillips 66 Petroleum – Specialty Chemicals (Borger, TX). Over the duration of the program, three lots of CAA compliant baseline gasoline were blended. The first lot (RF-A-BG) was used to develop an alternative method for generating the vapor condensate (test article) to be used in the 211(b) Rule testing. The second lot (API 99-01) was used to splash-blend each of the six gasoline/oxygenate blends and prepare the vapor condensate test articles for all the studies described in this series of papers. The oxygenates used were procured by Phillips 66 Petroleum from various commercial sources and included methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), t-amyl methyl ether (TAME), diisopropyl ether (DIPE), t-butyl alcohol (TBA), and ethanol (EtOH). The oxygen content of the various fuel blends was the maximum allowed under EPA regulations at the time of preparation. For MTBE, ETBE, TAME and DIPE the oxygen content target was 2.7 wt. %. For EtOH and TBA the oxygen content target was 3.7 wt. %. The third lot (API 02-08) of baseline gasoline was used to generate additional baseline gasoline vapor condensate to complete the chronic/carcinogenicity study.

Table 1
Baseline gasoline fuel properties.

Property	ASTM method	EPA specifications [a]	RF-A-BG [b]
API gravity	D 4052	57.4 ± 0.3	57.7
Sulfur, ppm	D 4294	339 ± 25	320
Benzene, volume %	GC	1.53 ± 0.3	1.44
RVP, psi	D 323	8.7 ± 0.3	8.7
Octane, (R + M)/2	D 2699 D 2700	87.3 ± 0.5	87.5
Distillation parameters:	D 86		
10%, °F		128 ± 5	126
50%, °F		218 ± 5	216
90%, °F		330 ± 5	332
Hydrocarbon type (volume %)	D 1319		
Aromatics		32.0 ± 2.7	31.7
Olefins		9.2 ± 2.5	11.6
Saturates		58.8 ± 2.0	56.7
Additive types:			Treat rate used (lbs/1000 barrels)
Required		Deposit control	107
		Corrosion inhibitor	5
		Demulsifier	2
		Anti-oxidant	5
		Metal deactivator	1
Permissible		Anti-static	0.5

[a] 40 CFR79.55.
[b] Phillips 66 petroleum data.

2.2. Determining headspace vapor compositions

The compositional target for the test articles made using the alternative method were determined by analyzing the equilibrium headspace of sealed 20 ml vials filled 40% full with baseline gasoline or the gasoline/oxygenate blends. This volume was consistent with the original 1994 CAA 211(b) rule requirement of an "evaporative emission generator" being 40% full at the start of the procedure. Duplicate samples were prepared and analyzed on the same day. The sealed vials were submerged up to the cap in a 130 °F water bath for 10 min at which time they were inverted three times and replaced for 5 min more. The headspace vapor composition was determined by gas chromatography (GC). A Hewlett Packard 19395A headspace sampler was programmed to withdraw a headspace sample at this time and transfer it through a heated line to a gas chromatograph (Hewlett Packard 5890 Series II) equipped with a non-polar fused silica capillary column. The injection volume of headspace vapor was 1 mL into 30 psi helium carrier gas at an injection temperature of 250 °C (split flow 200 mL/min). The oven temperature program is proprietary information.

The material eluting from the column was quantified using a flame ionization detector at 250 °C (H_2 30 mL/min; Air 300 mL/min). Data was collected by an EZChrom Data System and individual compounds identified by proprietary techniques (Chevron SE-30).

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