Chevron

Research and Technology

Fuel Blending, Headspace Analysis, and Benchtop Vapor Generation for an Alternative Evaporative Emissions Generation Procedure Under Clean Air Act Section 211(b)

Report to the American Petroleum Institute
Project HES1860-L-00870-BLEND

Chevron Research and Technology Company
October 20, 1997

Introduction

Chevron Research and Technology Company (Chevron), under the sponsorship of American Petroleum Institute (API), undertook a study of fuel blending, headspace analysis and benchtop vapor generation to develop data to support a petition for a change in the method of evaporative emissions generation under Clean Air Act Section 211(b). This study was conducted by Chevron's Analytical Sciences Unit and Toxicology and Health Risk Assessment Unit, 100 Chevron Way, Richmond, CA 94802.

Materials and Methods

Fuel Blending:
Fuel blending was done according to Chevron SOP ME-011-1. API 94-02 Gasoline was obtained by API from Phillips Petroleum (Lot S-424-A) and shipped to Chevron in 55 gallon steel drums. This gasoline was blended to meet the fuel specifications for CAA 211(b) (40 CFR part 80) including the additive package expected to be used in Tier One and Tier Two testing.

API 94-02 Gasoline was blended with the following oxygenate materials:

- Methyl Tertiary Butyl Ether (CAS 1634-04-4) from Aldrich Chemical
- Ethyl Alcohol (CAS 64-17-5) from Gold Shield Chemical
- Tertiary Amyl Methyl Ether (CAS 944-05-8) from Chevron
- Ethyl Tertiary Butyl Ether (CAS 637-92-3) from Phillips Petroleum
- Tertiary Butyl Alcohol (CAS 75-65-0) from Aldrich Chemical
- Diisopropyl Ether (CAS 108-20-3) from Aldrich Chemical

Each oxygenate was blended with API 94-02 gasoline by weight to achieve a final weight of 28387.5 grams (the weight of 10 gallons of API 94-02 at 60°F). Table 1 below outlines the fuel blending parameters that were used to determine the amount of material needed to make the required blends.

Table 1

	% Oxygen per Molecule	Finished Blend Wt. (grams)	Finished Wt % O Target	Oxygen Needed (grams)	Oxygenate Needed (grams)	Finished Blend Wt% Oxygenate*	Gasoline Needed (grams)	Purity of Oxygenate Used
94-02	0	28387.5	0	0	0	0	28387.5	
MTBE	18.2	28387.5	2.7	766.5	4211.5	14.84 ± 0.73	24176	99.80%
EtOH	34.8	28387.5	3.7	1050.4	3018.2	10.63 ± 0.88	25369.3	100%
ETBE	15.7	28387.5	2.7	766.5	4882.2	17.20 ± 3.13	23505.3	98%
TAME	15.7	28387.5	2.7	766.5	4882.2	17.20 ± 1.32	23505.3	99.20%
DIPE	15.7	28387.5	2.7	766.5	4882.2	17.20 ± 2.83	23505.3	98%
TBA	21.6	28387.5	3.7	1050.4	4862.9	17.13 ± 1.27	23524.6	99.50%

* Reproducibility determined from ASTM D4815-94a. Assume oxygenate purity of 100%.

The fuel oxygen content, Reid vapor pressure and boiling curve were determined by ASTM methods D4815-94a, D519, and D86, respectively, and the components were identified by gas chromatography (CRTC Test Method SE-30, Test Code 50105).

Headspace Analysis:
Headspace analysis was done according to Chevron SOP ME-019-0. For the analysis, 8.7 milliliters of API 94-02 gasoline and each of the oxygenate blends were put into 21.8 milliliter headspace vials. (This volume is consistent with the current 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 placed one at a time in a Hewlett Packard 19395A headspace sampler maintained at 130°F for 10 minutes, at which time they were inverted three times and replaced for 5 minutes more. The headspace sampler was programmed to withdraw a sample at this time and transfer it through a heated line to a gas chromatograph equipped with a capillary fused silica column coated with methyl silicone stationary phase, following CRTC Test Method SE-30, Test Code 50105. Compounds eluting from the column were detected by a flame ionization detector and identified by comparison to previously identifiec standards.

Benchtop Vapor Generation:
Benchtop vapor generations were done according to Chevron SOP ME-012-0. For the benchtop vapor generation, twenty liters (5.3 gallons) of a fuel blend were put into a fifty liter (13.2 gallon) distillation flask with a two inch sample port. (This volume is consistent with the current CAA 211(b) rule requirement of an "evaporative emission generator" being 40% full at the start of the procedure.) The vapor passed out of the port opening through a 6-inch glass riser attached to a

20-inch diagonal glass condenser and two sequential "overhead" cold traps. The condenser, collection vessel, and overhead traps were chilled with a dry ice-alcohol mixture. The sample was mixed and slowly heated to bring the vapor temperature to 130°F. Monitoring of the liquid and vapor temperatures was done continuously and recorded on the distillation run log as appropriate. If the volume of vapor condensate collected when 130°F vapor temperature was reached was less than three liters (15% of starting volume), the first collection sample was removed and heating continued until a second sample was collected to achieve a total volume collected of approximately three liters. Both samples (if necessary) were analyzed by gas chromatography (CRTC Test Method SE-30, Test Code 50105). API 94-02 gasoline was also used in this procedure with a starting volume of forty liters (10.6 gallons), to compare the impact of different starting volumes on vapor condensate composition.

Results

Appendix A contains all of the relevant data analysis in a series of Tables and Graphs.
Appendix B contains copies of the gas chromatography data of the fuel blends.
Appendix C contains copies of the gas chromatography data from the headspace analysis.
Appendix D contains copies of the vapor generation run logs.
Appendix E contains copies of the gas chromatography data from the vapor generations.
Appendix F contains copies of the protocol and protocol amendments.

Fuel Blending:
The concentration of each oxygenate in the finished fuel blends was measured by two methods, CRTC Test Method SE-30 and ASTM D 4815. Both methods gave similar results (page 1 of Appendix A) and demonstrated that the oxygenate content of the fuel blends meet the target specifications setout in Table 1. Changes in the base fuel's Reid Vapor Pressure (psi) after addition of oxygenate were consistent with the blending vapor pressure of the oxygenate used (page 2 of Appendix A). Detailed chemical composition of the base gasoline and each oxygenated blend is contained in Appendix B.

Headspace Analysis:
Analysis of the 130°F equilibrium headspace vapor from duplicate samples showed excellent agreement. Selected components of base gasoline and the oxygenate blends are displayed on page 1 of Appendix A. For the comparisons made in the rest of this report, the average of the duplicate samples was used. The equilibrium vapor composition at 130°F represents the desired composition for the sample obtained from the vapor generation procedure. More detailed results from the headspace analysis can be seen in each of the graphs contained in Appendix A. Copies of the gas chromatography data for the headspace analysis are contained in Appendix C.

Benchtop Vapor Generation:
The conduct of the vapor generations were satisfactory. Mass balance calculations found most procedures lost less than 1% of the starting weight. Only the ethanol and ETBE blends exceeded 1% (page 2 of Appendix A). With every fuel blend, when the vapor temperature reached 130°F, the temperature of the liquid was greater than 130°F (page 2 of Appendix A). The liquid/vapor differential was 18°F for the ethanol blend and 59°F for the TAME blend. Appendix E contains copies of the vapor generation run logs.

Vapor generation procedures for gasoline (API 94-02) were conducted with the benchtop kettle either 40% or 80% full. The volume of sample in the kettle made a surprisingly large impact on the composition of the vapor condensate (page 1 and 3 of Appendix A). Data from the API Gasoline Developmental Study (API Report TR412) which prepared a vapor condensate sample from 94-02 gasoline in an industrial 1000 gallon kettle has been included with these results for comparison (pages 1 and 3 in Appendix A). Increasing the sample volume to 80% of the benchtop kettle gave results very similar to those from the 1000 gallon industrial kettle. The 1000 gallon kettle is expected to be used for any full scale preparation work for toxicology testing under 211(b) regulations. The 130°F vapor condensate from the 80% benchtop or the 1000 gallon kettle have less C4s than the 130°F equilibrium headspace, but the C5 through C10 hydrocarbons are well represented.

As part of the benchtop vapor generations, a second sample of condensate was collected to bring the total volume collected to 3 liters (15%). This second sample was analyzed and the results combined with the 130°F vapor condensate (pages 4 and 5 in Appendix A). Increasing the volume of condensate improves the match with the 130°F equilibrium headspace.

The benchtop vapor generations for the oxygenate fuel blends were only conducted with the kettle 40% full. The amount of oxygenate recovered in the 130F vapor condensate varied significantly from the amount of oxygenate recovered in the 130°F equilibrium headspace (page 1 of Appendix A). While MTBE and ethanol blends gave comparable results, most often the oxygenate was under-recovered in the condensate compared to the headspace value. Increasing the volume of material in the kettle to 80% should improve the yield. A comparison between the vapor condensate and the 130°F headspace for each of the oxygenates are found in Appendix A as follows:

MTBE -- pages 6 and 7
TAME -- pages 8 and 9
DIPE -- pages 10 and 11
ETBE -- pages 12 and 13
Ethanol -- pages 14 and 15
TBA -- pages 16 and 17

For two of the oxygenate blends, a second sample was collected to reached approximately three liters of condensate. For the DIPE blend, the second sample was 436 milliliters and contained 22.26% DIPE by weight. The addition of the second sample raised the total percentage of DIPE collected to 15.37% (page 18 of Appendix A). For the TBA blend, the second sample was 313 milliliters and contained 31.24 % TBA by weight. The addition of the second sample raised the total percentage of TBA collected to 6.47% (page 19 of Appendix A). These results indicate that by collecting more vapor condensate, the amount of oxygenate recovered can be increased to better match the 130°F equilibrium headspace value. The C4 to C10 hydrocarbons also showed a better match with the 130° equilibrium headspace values when additional vapor sample was collected.

Appendix E contains copies of the gas chromatography data from the vapor generations.

Conclusions

These data provide sufficient justification for advocating a change in the Clean Air Act 211(b) requirements for generating evaporative emissions for animal toxicology testing.

- The starting volume of gasoline in the prescribed 211(b) methods is given as "40% full". The experiments with base gasoline show that the starting volume does influence the composition of the vapor. Filling the benchtop kettle to 80% full or using a 1000 gallon industrial kettle produced a vapor sample that is more like the 130°F equilibrium headspace vapor composition.

- The prescribed 211(b) methods state that no more than 7% of the starting volume of gasoline will be removed during test sample generation. The experiments that collected additional vapor beyond the 130°F cutoff demonstrate that increasing the amount of vapor collected improves the match with the equilibrium vapor composition.

- The prescribed 211(b) methods state that the temperature of the fuel and vapor are to be 130° ± 5°F. These experimental data confirm that the liquid fuel temperature is always greater than the vapor temperature. The minimum differential was 18°F for the ethanol blend. For the oxygenate with the highest boiling point, TAME, the differential was 59°F. If required to maintain a 130°F liquid temperature, there would not be enough vapor to conduct the toxicology studies described in Tier 2 of CAA 211(b).