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Energy & Environmental Research Center

EFFECT OF ETHANOL DENATURANT ON GASOLINE RVP (REVISED)

Topical Report

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EFFECT OF ETHANOL DENATURANT ON GASOLINE RVP (REVISED)

1.0 INTRODUCTION

The Clean Air Act (CAA) Amendments of 1990 require further reduction in gasoline Reid vapor pressure (RVP) to reduce pollution. Our research focused on characterizing the effect of ethanol denaturant and water on the RVP of the final ethanol-blended fuel. Anecdotal stories tell of up to a 0.5-psi effect of ethanol denaturant on the RVP of the finished ethanol-blended gasoline. Additionally, earlier Energy & Environmental Research Center (EERC) data indicated water could have a significant effect on RVP. It was necessary to scientifically verify these effects using acceptable laboratory protocols.

Environmental Protection Agency. An important aspect of this study was the development of the laboratory testing procedures that will lead to data acceptable to rule-making organizations such as the U.S. Environmental Protection Agency (EPA). We have maintained a dialogue with the EPA to ensure acceptable laboratory protocols.

Denaturants. The Code of Federal Regulations (27 CFR 21) specifies the alcohol denaturants authorized for fuel uses. Of these, we selected unleaded gasoline, rubber hydrocarbon solvent (natural gas liquids), kerosine, and methanol for use in this study.

Experimental Design. The first series of tests established the base RVP and water content of the starting ethanols, natural gas liquids, regular unleaded gasoline, methanol, and kerosine. Since many prior gasoline studies have been based on Indolene HO III as a model fuel for unleaded gasoline, our second test matrix used indolene to produce E10 blends. The form of the indolene matrix was repeated with a local sample of regular unleaded gasoline obtained "at the pump" as the third matrix. The fourth experimental matrix was performed on a premium unleaded gasoline. As the magnitude of the water effect became apparent, additional water tests were performed. EPA's Motor Vehicle Emissions Laboratory, Ann Arbor, Michigan, supplied its current standard gasoline, "CAA Baseline gasoline."

2.0 PROTOCOLS

A key objective of this study was to develop laboratory protocols that would improve the acceptability of the data by regulatory agencies, such as EPA. Mr. Ronald Timpe (EERC), met twice with Mr. Carl Scarbro, EPA, in Ann Arbor, in addition to numerous telephone conversations. We feel that our protocol achieves this key objective. In fact, there are areas where our protocol is more stringent than that used by EPA's Ann Arbor Motor Vehicle Emissions Laboratory (see Appendix A). This is critical. If we are to influence EPA with our results, our protocols must be above reproach.

3.0 FUEL WEATHERING

Two gallons of the EPA CAA fuel was stripped of a portion of the light ends to reduce the RVP to roughly 7.0 to 7.5 psi. A glass carboy containing the fuel was maintained at 100°F in a temperature-controlled water bath. A 200-cc/min purge of

nitrogen was used to carry the vapors over to a dry ice-isopropanol cold trap for collection.

A stripping test was used to determine how much of the light ends needed to be removed in order to get to the desired RVP. It was estimated from previous data that about a 3 wt% removal of lights should bring the RVP down from a starting point of 8.8 psi to around the 7-psi desired level. It was found that a removal of 2.79 wt% lowered the RVP to 6.8 psi. The remaining gasoline was stripped to a lesser extent.

4.0 CONCLUSIONS

Care has been taken to ensure the acceptability of the data generated by this study. While a more complete analysis of the data is being prepared for the peer-reviewed technical publication, four definite, and scientifically significant, conclusions can be made:

1. In all cases (nine experimental series) where water was added to an ethanol blend, the RVP increased. This positive influence on RVP may indicate that the existing body of RVP data drawn from at-the-pump fuels may include an unknown measure of water-induce vapor pressure (see Figure 1).

For any sampling of at-the-pump gasolines, it is reasonable to expect a certain degree of water contamination. However, the use of gas-line antifreezes acknowledges the issue of water contamination in many gasoline situations, not just those concerning ethanol blends.

2. The different denaturants used in this study produced different final RVPs. While the magnitude of the denaturant effect did not meet anecdotal stories, the differences were significant. It can be concluded that a better matching of the denaturant to the base fuel will lead to a reduction in the overall average RVP of E10 fuels. Insufficient data are available to allow us to determine the best choice of denaturant (see Figure 2).
3. From weathering tests of the EPA CAA baseline gasoline, removal of little more than 1% of the fuel volume resulted in the reduction of the base RVP by 1 psi. This result could have a profound effect on the impact of fuel weathering and commingling (see Table 1).
4. The use of incrementally larger amounts of ethanol (in the E12 to E15 range) may yield a further reduction in RVP. While this improvement is likely to only be around 0.1 psi, any area for RVP improvement should be considered (see Figure 3).

From our initial statistical analysis, significant differences appear to be justified for changes as small as 0.1 psi. This is lower than the generally accepted 0.3 psi.

5.0 FUTURE RECOMMENDATIONS

Samples of all starting materials have been submitted for detailed chemical characterization by gas chromatography (the results will be presented in the technical publication). It is recommended for future work to characterize the various vapor phases produced by each blend. With a reduction of RVP in the aforementioned areas, confirmation will be needed to show a concomitant reduction in ozone-forming potential.

It is also recommended, from the brief fuel stripping data available, that this area be investigated further. Commingling, the issue of mixing fuels leading to potential noncompliance, could underestimate the effect of weathering on fuel composition. It is possible that commingling could represent a much more widespread problem than merely an ethanol versus nonethanol blend issue.

Additionally, it appears our data are consistent with the American Petroleum Institute (API) reporting of an increase in the ethanol bump at lower blendstock RVP. If RVP continues to be a key issue surrounding the use of ethanol blends, and as the trend continues to reduce fuel RVP, it will become necessary to understand the chemical basis for this effect. Our indication is that the formation of azeotropes could represent a plausible explanation. If so, ethanol antagonists could be identified in gasoline. Further work is needed.

Lastly, investigation into effect of temperature (in the 70° to 130°F range), combined with the assessment of RVP of ethanol blends between E10 to E85, should be performed systematically to help explain ethanol's RVP effect. It is anticipated that additional remediation strategies can be identified to maintain the role ethanol can play in producing safe, domestically renewable transportation fuels.

6.0 ACKNOWLEDGMENTS

Project funding was provided by the National Corn Growers Association and U.S. Department of Energy through the joint venture program at the Energy & Environmental Research Center, University of North Dakota. The project is indebted to Carl Scarbro, EPA Motor Vehicle Emissions Laboratory, Ann Arbor, Michigan, who shared his experience and provided insight to assist us in making technical decisions. The authors would like to thank Amoco Oil Company (Naperville, Illinois), Archer Daniels Midland ethanol plant (Walthalla, North Dakota), and Alchem, Inc. (Grafton, North Dakota), for furnishing key starting materials (gasoline, denaturant, and ethanol) without charge. Lastly, we would like to thank Ron Kulas, Dan Stanley, and Mel Pederson for their tireless efforts in the laboratory.

Figure 1. Effect of water addition on RVP of EPA CAA E10.

Figure 2. Effect of denaturants on RVP of premium unleaded E10.

Figure 3. RVP of E10, E12, and E15 using three fuels.

TABLE 1

Weathering of EPA CAA Baseline Gasoline (starting RVP 8.8)

	Wt% Lights Removed	Wt% Gasoline Recovered	Total Recovery %	Resulting RVP
Sample 1	2.79	96.72	99.51	6.8
Sample 2	1.79	98.21	99.92	
Sample 3	1.15	98.61	99.76	7.25 ¹

¹ Samples 2 and 3 were combined.

APPENDIX A

**SUMMARY OF SAMPLE PREPARATION
AND RELATED DATA**

SUMMARY OF SAMPLE PREPARATION AND RELATED DATA

The procedures followed in this study are detailed here as a service to the reader as a result of observations made during the study. Collecting, storing, blending, and analyzing samples appears on the surface to be straightforward, especially in light of the details that appear in the American Society for Testing and Materials (ASTM) methods and in the Federal Register (FR). However, although following the printed matter with extreme care, questions arose during each segment of the study that required answers that were not immediately obvious from the references. This section of the report includes information that, on the surface, may seem obvious, but is integral to the successful acquisition of meaningful RVP data.

OBTAINING THE FUEL

Gasolines and denaturants used in this study were of two types, commercially available gasoline and specialty research gasoline. The specialty fuels included Indolene H.O. Motor Fuel III from Amoco Oil Company, Naperville, Illinois, and Environmental Protection Agency Clean Air Act (EPA CAA) fuel from EPA's Motor Vehicle Emissions Laboratory, Ann Arbor, Michigan. Ethanol and natural gas liquid denaturant were provided by Archer Daniels Midland (ADM) Walhalla, North Dakota, and regular unleaded gasoline (RUG) denaturant was obtained from Alchem, Inc., Grafton, North Dakota.

At-the-pump regular and premium gasolines were purchased from Highway Host Amoco service station, Grand Forks, North Dakota. The gasoline was collected in precleaned 1-liter Boston round bottles by bottom-filling the bottle through an aluminum nozzle extender described in 56FR52316, October 18, 1991, to 75%–80% capacity after more than 10 gallons of fuel had been dispensed through the hose. The protocol followed is detailed in ASTM D4057.

STORING THE FUEL

The indolene and 15 gallons of the EPA CAA were shipped in sealed 5-gallon cans by air transportation for receipt the next day. Another 5 gallons of the EPA CAA fuel was received in individual 1-gallon cans. The unopened sealed cans were stored in an air-conditioned room at 20°C until use within a few days. The ethanol, regular unleaded gasoline denaturant, and the natural gas liquid denaturant were collected in 5-gallon Eagle™ UI50 S Type I safety cans and refrigerated at 0°C until use. In all cases, the contents of the safety cans developed a vacuum upon cooling and were under vacuum when opened for dispensing.

The at-the-pump gasolines were brought immediately to the Energy & Environmental Research Center (EERC) and placed in freezers at 0°C for use the following day.

DISPENSING THE FUEL

The specialty fuels, i.e., indolene, EPA fuel, and ethanol, and denaturants, i.e., natural gas liquids (NGL) and RUG, used in this study were received in 5-gallon containers as described above. Just prior to use, the entire contents of each container was transferred to 1-liter precleaned Boston brown bottles. The transfer was accomplished in the freezer by bottom-filling numbered bottles through a 1/4-inch-O.D. stainless steel tube. The transfer tube was inserted through an aluminum covered stopper to the bottom of the fuel can and the outlet was sealed by firmly placing the stopper in the hole. Argon flow was used to increase the pressure within the can to slightly above ambient to force the liquid from the can into the bottles. The order of filling the bottles was recorded in case of variations in the sample during the transfer. The bottles were sealed and stored in the freezer at 0°C until use.

At-the-pump regular unleaded and premium gasoline samples were collected according to the EPA guidelines recorded in 58FR14480, March 17, 1993. Water used in "spiking" gasoline samples with various water concentrations was Fisher HPLC grade.

BLENDING THE FUEL

Class A glassware was used throughout this project wherever accurate volumetric measurements were required. Precleaned amber Boston brown bottles purchased specifically for this project and certified cleaned according to EPA wash procedure, as set forth in the EPA Statement of Work "Specifications and Guidance for Obtaining Contaminant-Free Sample Containers," were used as sample collection vessels and containers throughout. All bottles and flasks were dried in a drying oven at 200°C for at least 15 minutes, capped, and brought into the freezer. If, upon cooling to freezer temperature, moisture of any kind was noted on the inside of the bottle, the drying procedure was repeated.

All samples were prepared in a walk-in freezer at a temperature of -15°C and a relative humidity of 80%–100%.

Ethanol (750 mL) was measured in Class A volumetric flasks and transferred to tared 1-liter precleaned Boston brown bottles. Denaturant was added using either a 15-mL pipet for the 2% level or a buret for the 5% addition. The bottles were capped, inverted 10 times, and allowed to stand for 1–2 hours before addition of water or dispensing to 4-oz Boston brown bottles for Karl Fischer (K-F) and RVP testing.

When adding water, the 4-oz tared bottles were filled to the 75% full level with the blended gasoline, weighed, the desired amount of water added (0.2% or 0.4% by weight), and the bottles capped tightly until analyzed.

ANALYZING THE FUEL

Reid Vapor Pressure Equivalent. The method of vapor pressure determination in the "as-received" samples and the blended samples was as described in ASTM 5191 for the Grabner CCA-VPS fully automatic vapor pressure instrumentation. Since these data

provided the bases for the conclusions of this study, the procedure for obtaining the RVP data will be detailed here.

General Procedure. The Reid vapor pressure was measured in compliance with ASTM Method D5191-91 "Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method)" using a Grabner Instruments CCA-VPS, EPA-approved instrumentation.

1. Sampling (see ASTM D5191 Section 8)
 - a. Samples were received in tightly sealed Boston round bottles approximately 75% to 80% full.
 - b. Samples were examined for phase separation upon receipt and just prior to analysis.
 - c. Samples were received cold and stored in a refrigerator at 0°C. The samples were removed from the refrigerator and placed in an ice or water/glycol solution at 0°C for at least 4 minutes prior to analysis.
 - d. Samples were air-saturated according to ASTM D5191 Section 8.4. Each sample was cooled for 4 minutes, opened momentarily, and vigorously shaken for 1 minute, then the procedure was repeated twice more.
 - e. Samples were again examined for phase separation or cloudiness before injection into test chamber (ASTM D5191 Section 8.5).
2. Preparation of Apparatus:
 - a. The Grabner chamber was rinsed with air and the chamber evacuated before testing for a day was started.
 - b. The cell was cleaned (rinsed with air and evacuated to 0.5 mm Hg or less) after each three samples. The first test performed after the cleaning was the sample with ambient water. The cell was evacuated while cleaning until the Grabner gave a stable reading of 0 psi for 5 min.
 - c. As specified in 9.1 of ASTM D5191, the manufacturer's suggestions for cleaning the cell were followed (page 16, Section 5.5 of the Grabner CCA-VPS Operation Manual, October 6, 1991).
3. Sample Introduction
 - a. The sample was taken from the ice or glycol bath following air saturation and cooling as prescribed in Section 8.4, ASTM D5191. The bottle was opened, and the sample introduction tube was inserted into the sample container.
 - b. Two tests were performed per sample in sequence. Therefore, the sample was kept on ice while introduction took place. The sample introduction tube was put through a hole in a lid, to minimize volatiles losses between tests.
4. Calibration and Quality Control
 - a. The instrument was last calibrated on the last day of testing according to the method described in the Grabner operator's manual.
 - b. Standards used on Grabner were 3-methylpentane and 2,2-dimethylbutane. They were treated the same way as the samples, and run daily, or every nine samples, or both. They verified the calibration of the Grabner as they were within the control limits set forth in the 58FR14489, March 17, 1993. Those specifications are as follows:

3-methylpentane 6.86 psi < P_{tot} < 7.26 psi

2,2-Dimethylbutane 10.64 psi < P_{tot} < 10.93 psi.

- c. The calibration was also checked periodically against a mercury manometer to ensure that the instrument reading varied < 0.02 psi from the manometer reading.

Karl Fischer Water Analysis: The method of water determination in the as-received samples and the blended samples was as described in ASTM D1744-83. K-F reagent solution, reagent-grade K-F methanol, and a commercial K-F coulometric titration apparatus manufactured by Lab Industries were used to measure the water content.

A "constant" or "titer" was established to determine the reagent strength of the K-F reagent. Initially, 50 mL of methanol was introduced into a glass cell in which the coulometer electrodes were immersed. Inherent water in the methanol was reacted by adding K-F reagent (titrant) until the indicator needle came to rest in the "neutralized" zone and remained there in a stable manner. A weighed drop of water was then injected into the methanol. The coulometer responded with a needle deflection into the "water" zone. K-F reagent was then added from the buret until the water content was neutralized as indicated by the coulometer. The reactivity or "neutralizing" effect of the K-F reagent was then determined by dividing the weight of the drop of water in milligrams by the amount of K-F reagent titrated in milliliters. The number determined is the titer or constant to be used in the formula that establishes the water content in the samples to be tested.

Since the water content of gasoline samples tends to be extremely low (<100 ppm), it was necessary to inject 10 mL of gasoline, or blended gasoline, rather than 1 mL into the cell to reduce the uncertainty in the measurement. The gasoline was drawn into a 10-mL volumetric pipette and injected into the cell. The weight of the sample was established by determining the specific gravity of the sample:

$$\text{specific gravity} \times \text{volume} = \text{weight}$$

The water content of the gasoline was neutralized with K-F reagent. The % water of the gasoline sample was then determined using the following calculation:

$$(\text{titer} \times \text{mL titrant/sample weight in mg}) \times 100 = \% \text{ H}_2\text{O in sample}$$

Duplicate water analyses were obtained for each sample. Both results were recorded and the average of the two was reported. The cell was recharged with methanol and neutralized after any two successive samples.

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Figure 2. Effect of denaturants on RVP of premium unleaded E10.

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