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Gasoline toxicology: Overview of regulatory and product stewardship programs

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ABSTRACT

Significant efforts have been made to characterize the toxicological properties of gasoline. There have been both mandatory and voluntary toxicology testing programs to generate hazard characterization data for gasoline, the refinery process streams used to blend gasoline, and individual chemical constituents found in gasoline. The Clean Air Act (CAA) (Clean Air Act, 2012: § 7401, et seq.) is the primary tool for the U.S. Environmental Protection Agency (EPA) to regulate gasoline and this supplement presents the results of the Section 211(b) Alternative Tier 2 studies required for CAA Fuel and Fuel Additive registration. Gasoline blending streams have also been evaluated by EPA under the voluntary High Production Volume (HPV) Challenge Program through which the petroleum industry provide data on over 80 refinery streams used in gasoline. Product stewardship efforts by companies and associations such as the American Petroleum Institute (API), Conservation of Clean Air and Water Europe (CONCAWE), and the Petroleum Product Stewardship Council (PPSC) have contributed a significant amount of hazard characterization data on gasoline and related substances. The hazard of gasoline and anticipated exposure to gasoline vapor has been well characterized for risk assessment purposes.

1. Introduction

Gasoline is a liquid hydrocarbon fuel that is used in spark ignition engines for automobiles, tractors, lawn-mowers, snowmobiles, jet skis, and dozens of other types of equipment. Modern gasoline, the focus of this review, is the result of significant evolution over the past century. Improvements in refining practices, engine design, and better understanding of the health and environmental impacts have all worked to create the version of gasoline now on the market. Many of these design and manufacturing improvements either resulted in, or were the result of, a wide range of standards and regulations to ensure a high level of product consistency in the marketplace, which is essential given the complexity of modern engines.

In the U.S., gasoline is a blended product (i.e., mixture), which is not listed on the Toxic Substances Control Act (TSCA) Chemical Inventory. However, the substances that are used to blend gasoline – such as refinery process streams – are on the TSCA Inventory (API, 1983; USEPA, 1995a). In the European Union (EU), gasoline is an unique substance on the EU Chemical Inventory (ESIS, 2014) and is identified by the Chemical Abstract Service (CAS) registry number "86290-81-5," the CAS name "Gasoline," and the CAS definition "A complex combination of hydrocarbons consisting primarily of paraffins, cycloparaffins, and, aromatic and olefinic hydrocarbons having carbon numbers predominantly greater than C3 and boiling in the range of 30–260 °C (86–500°F)."

Whether defined as a substance or a mixture, gasoline is blended from various refinery process streams to achieve the required physical property, performance, and composition specifications. Gasoline typically contains several hundred individual hydrocarbon constituents in the C4–C12 carbon-range and several additives in the part-per-million (ppm) concentration range that prevent fuel degradation (i.e., antioxidant, metal deactivator) or improve engine performance (i.e., detergent) (ASTM, 2010). The refinery streams that comprise the bulk of the gasoline volume are in a class of substances referred to as **U**nknown or **V**ariable compositions, **C**omplex reaction products and **B**iological (UVCB) substances (USEPA, 1995b).

There have been both mandatory and voluntary testing programs to generate hazard characterization data on gasoline and refinery process streams. The Clean Air Act (CAA) (Clean Air Act, 2012: § 7401, et seq.) provides the U.S. Environmental Protection

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Agency (EPA) the authority to regulate emissions of gasoline. The wide scope of that authority is reviewed in detail elsewhere in this supplement (Swick et al., 2014). The specific authority under CAA Section 211 (Clean Air Act, 2012: § 211) is reviewed in this paper. EPA also has authority under the Toxic Substances Control Act (TSCA) (Toxic Substances Control Act, 2012: § 2601, et seq.) to require hazard screening tests under Section 4. Several instances of test rules for gasoline components issued under TSCA Section 4 are reviewed in this paper. EPA also initiated a voluntary program asking industry to develop and make publically available data on high production volume (HPV) chemicals (USEPA, 1998). HPV chemicals are those substances that are manufactured or imported into the U.S. in amounts exceeding one million pounds per year. Virtually all refinery process streams used to make gasoline meet this criterion for HPV chemicals.

EPA also initiated the Voluntary Children's Chemical Evaluation Program (VCCEP) in December 2000 to assess the risks associated with potential children's exposure to approximately 20 large volume chemicals. Industry funded the data collection and an independent panel conducted the review. Four of the chemicals reviewed in the VCCEP program are constituents in gasoline: benzene, toluene, ethylbenzene, and xylenes (BTEX).

Product stewardship efforts by individual companies and by industry trade associations have also contributed significantly to the available hazard characterization data on gasoline, its blending streams, and various chemical constituents. The American Petroleum Institute (API) and the European organization CONCAWE (Conservation of Clean Air and Water Europe) have also conducted studies on various petroleum products including gasoline. Another organization is the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG), which was formed as a coalition of industry and government groups to establish appropriate soil clean-up levels after spills of petroleum products like gasoline, jet fuel, diesel fuel, etc. The Petroleum Product Stewardship Council (PPSC) comprised of toxicologists from AMOCO, ARCO, BP, Chevron, Mobil, Texaco, and Unocal conducted hazard characterization studies on the blending streams used in gasoline and diesel fuels. Individual companies have also conducted and published relevant hazard studies on gasoline blending streams.

These regulatory and product stewardship efforts are described in more detail below, with the goal of providing references for the numerous reports and peer-reviewed publications that have resulted from that activity.

2. Gasoline studies mandated by the Clean Air Act

Section 211 of the Clean Air Act (CAA) gives the U.S. Environmental Protection Agency (EPA) broad authority to regulate the content and characteristics of gasoline and gasoline additives (Clean Air Act, 2012: § 7545). EPA's information requirements to obtain registration to sell fuel and fuel additives are quite strict and follow a three-tiered approach. (See Fig. 1).

2.1. 211(b) Research Group

In response to the tiered registration requirements, the American Petroleum Institute (API) organized the 211(b) Research Group (Research Group). The Research Group is an unincorporated group of fuel, fuel oxygenate, and fuel additive manufacturers affiliated by contractual obligation to meet the Tier 1 and Tier 2 testing requirements of Sections 211(b)(2) and 211(e) of the Clean Air Act (Clean Air Act, 2012: §§ 211(b)(2) and 211(e)). EPA has not yet initiated any Tier 3 actions under the rule.

The 211(b) Research Group's purpose was to address two of the three categories of fuel outlined in the 211(b) Rule (Registration of Fuels and Fuel Additives, 2013: § 79.56). The Research Group tested: (1) "baseline" fuel groups that contain no elements other than carbon, hydrogen, oxygen, nitrogen, and sulfur, and gasoline containing less than 1.5% oxygen by weight, and diesel containing less than 1.0% oxygen; and (2) "non-baseline" fuel groups that 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 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.

2.2. Section 211(b) Tier 1 Fuel and Fuel Additives Hazard Characterization Program

Tier 1 requirements included a literature search of available studies for health and welfare effects of substances in diesel exhaust, gasoline exhaust, and gasoline evaporative emissions. To help fulfill these requirements, the Research Group contracted with EA Engineering, Science & Technology, Inc. to conduct this search. Twelve bibliographic databases were selected for searching on the basis of content, scope, and relevancy to this effort. Databases were searched back either 30 years or to their origins for information on health or welfare effects on the following emission entities: diesel fuel exhaust, gasoline evaporative emissions, and gasoline exhaust, as the three whole (primary) emissions; select fractions or classes of compounds (16) associated with these emissions (ethers, alcohols, hydrocarbons, ketones, and aldehydes as "speciated emissions" along with 11 select naphtha fractions); and numerous individual chemicals (173) found in these three primary emissions. For select chemicals (approximately 20) having enormous information bases in the open literature, comprehensive reviews were used to identify prior relevant studies, with literature searches providing information on more recent, post-review studies. Unpublished studies provided by Research Group member companies were also reviewed. Information from studies identified as relevant and appropriate was then extracted to summary tables (up to 15 combined health and welfare effects tables may exist per chemical or whole emission) for a wide variety of health or welfare effects. Study summaries were organized into a single report and submitted to EPA (EA Engineering, 1997) along with completed copies of the articles/studies.

To further fulfill Tier 1 requirements, the Research Group contracted with Southwest Research Institute to conduct vehicle emissions testing for the gasoline baseline and non-baseline fuels/fuel additives (F/FAs), and to conduct a literature review to characterize diesel exhaust emissions from heavy-duty vehicles.

For the gasoline F/FAs, exhaust and evaporative emission measurements were conducted using a 1996 Toyota Camry operating on a baseline ("industry average," RF-A) gasoline and six gasoline fuels each splash blended with specific oxygenates (EtOH, MTBE, ETBE, TAME, TBA, and DIPE). The exhaust emissions portion of the test matrix consisted of triplicate Federal Test Procedure (FTP) emissions tests with the vehicle operating in each of three different configurations. The three configurations included: (1) original equipment manufacturer's configuration; (2) without catalytic converter; and (3) without evaporative emission canister. One-hour diurnal heat build and hot-soak loss evaporative emission tests were conducted for test configurations 1 and 3 (Research Group, 1997).

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