Response to EPA's Hazard Characterization of the Refinery Gases Category

The American Petroleum Institute Petroleum HPV Testing Group

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The following comments are in response to EPA's Hazard Characterization (HC) for the Refinery Gases Category (U.S. EPA, 2011). This Category was sponsored by the American Petroleum Institute (API) Petroleum HPV Testing Group (Testing Group) as part of EPA's HPV Chemical Challenge Program (www.petroleumhpv.org).

Below is EPA's generic table of content for all the HPV Hazard Characterizations they have prepared, including Refinery Gases. The Testing Group's comments are found on the page numbers indicated below.

Summary

1. The EPA hazard characterization for several Petroleum HPV Categories including Refinery Gases, refers to the category members as complex mixtures when in fact they are Class 2 UVCB substances. (HC pages 5, 12, 17, 35, 36, 54, 175)

Substances on the US TSCA Inventory are divided into two classes for ease of identification (EPA 1995). Class 1 substances are those single compounds composed of molecules with particular atoms arranged in a definite, known structure. However, many commercial substances that are subject to TSCA are not Class 1 substances, because they have unknown or variable compositions or are composed of a complex combination of different molecules. These are designated Class 2 substances. Class 2 includes substances that have no definite molecular formula representation and either partial structural diagrams or no structural diagrams. These are the "UVCB" substances (Unknown or Variable compositions, Complex reaction products and Biological materials). An example of this kind of substance is given below.

CAS Number: 68478-00-2
CAS Name: Gases (petroleum), recycle, hydrogen-rich
CAS Definition: A complex combination obtained from recycled reactor gases. It consists primarily of hydrogen with various small amounts of carbon monoxide, carbon dioxide, nitrogen, hydrogen sulfide, and saturated aliphatic hydrocarbons having carbon numbers in the range of C1 through C5.

Petroleum substances are subject to nomenclature rules developed jointly by the U.S. EPA and the American Petroleum Institute (EPA, 1995b). In that guidance document, EPA adopts the definitions of petroleum process stream terms provided in API's published reference document Petroleum Stream Terms Included in the Chemical Substance Inventory under TSCA (1983, reprinted in 1985). The Stream Terms definitions include the CAS definition and registry number, the source of the substance and process (i.e., last refining step), short name, indication of carbon number, and indication of distillation range (or other appropriate characteristic). Therefore all members of the [name] Category are UVCB substances, not mixtures, under EPA's nomenclature guidance.

4. Hazard to the Environment

The EPA Hazard Characterization for the Refinery Gases Category was divided into four subcategories for the evaluation of ecotoxicity endpoints. Subcategories I-III were found to have no data gaps, and the existing data and technical summaries proved adequate for describing the potential aquatic hazards for these gas mixtures. Subcategory IV included 25 CAS RN that contained carbon monoxide in the gas mixtures. Owing to the lack of ecotoxicity data for carbon monoxide, the hazard to the environment for the sponsored streams in Subcategory IV containing carbon monoxide (>2%) could not be determined. Consequently, data gaps were identified for acute toxicity to fish and aquatic invertebrates and toxicity to aquatic plants.

The Testing Group considers aquatic toxicity testing of refinery gases that contain carbon monoxide as unnecessary and scientifically unjustified. All refinery gases in this category are produced in petroleum refineries as the light end fractions of numerous distillation and cracking processes. They are comprised of predominantly one to four carbon atom hydrocarbons and inorganic components. These gases exist as substances in closed systems in the refinery, with

none being sold a finished products because of one or more constituents makes them unsuitable for commercial sale. Potential emissions at these sites would be to the atmosphere and would partition from that environmental compartment in concert with their specific unique physicochemical attributes. Emissions directly to other environmental compartments would be highly unlikely owing to these constituents existing as gases at relevant environmental conditions

A determination of the potential for the gaseous streams containing carbon monoxide (>2%) to elicit aquatic toxicity can be made in a manner similar to that put forth in the Sponsor's Category Analysis Document (CAD) for other constituents of concern in these refinery gases. For refinery gases, key components were identified that could elicit aquatic toxicity, and those components were used in a Level 3 fugacity model to assess their environmental distribution resulting from emissions. The distribution factors were then taken into account and concentrations in a unit water body (2×10^{11} m^3) were calculated. These predicted exposure concentrations were then compared to toxicological effects data for the specific constituent in order to conclude whether a potential exists for adverse environmental effects. For environmental distribution modeling, carbon monoxide was used in a Level 3 fugacity model (Mackay et al 1996) adapted for use in EPA's EPI Suite model programs (EPA 2008). This model cannot assess mixtures of substances such that occur in these refinery streams. Therefore, the resulting calculations reflect the concentration of carbon monoxide that may partition to water following release to the atmosphere (default value of 1000 kg/h for one hour) of the pure gas. The key components and resulting calculations are shown here.

	Carbon monoxide
Water Solubility, mg/L	3392
Henry's LC, atm-m^3/mol	9.33×10^{3}
Mass amount in compartment, %	
air	100
water	2.44×10^{-7}
soil	3.59×10^{-3}
sediment	5.82×10^{-10}
Half-life in compartment, hr	37420
air	360
water	720
soil	3240
sediment	
Calculated concentration in water, mg/L	1.2×10^{-14}

The key finding in the above scenario is that emissions of carbon monoxide to air will remain in the air with virtually zero partitioning to other environmental compartments. However, using the information to calculate the concentration in the model unit body of water shows an exceedingly small concentration that can be compared to ecotoxicity data.

The lone aquatic toxicity data for carbon monoxide cited in EPA'S ECOTOX database was of a one-hour exposure to rainbow trout that reported an LC100 of 75 mg/L. This was reported in

1917, and due to the lack of details, the age of the study, and absence of analytical concentration verification, this can only be considered anecdotal information. Therefore, the following aquatic toxicity values were estimated using the ECOSAR QSAR model.

Fish 96-h LC50 = 35 mg/L
Invertebrate 48-h EC50 = 19 mg/L
Algal 96-h EC50 = 8.3 mg/L

The difference between these toxicity endpoints and the calculated concentration in water is orders of magnitude and lends confidence to the conclusion that no adverse effects to aquatic organisms would occur from atmospheric emissions of refinery gases containing carbon monoxide.

References cited in this response to EPA's HC for the Refinery Gases Category

Toxic Substances Control Act Inventory Representation for Chemical Substances of Unknown or Variable Composition, Complex Reaction Products and Biological Materials: UVCB Substances (March 29, 1995a); available from http://www.epa.gov/oppt/newchems/pubs/uvcb.txt

Toxic Substances Control Act Inventory Representation for Certain Chemical Substances containing Varying Carbon Chain Lengths (Alkyl Ranges Using the Cx-y Notation) (March 29, 1995b); available from: http://www.epa.gov/oppt/newchems/pubs/alkyl-rg.txt

Mackay et al. 1996. Evaluating the environmental fate of a variety of types of chemicals using the EQC model. Environ Toxicol Chem 15:1618-1626.
U.S. Environmental Protection Agency. 2008. Estimation Programs Interface (EPI) Suite™ V4.0. Washington, DC.

U.S. EPA (2011). Screening Level Hazard Characterization of High Production Volume Chemicals; Refinery Gases Category. http://www.epa.gov/chemrtk/hpvis/hazchar/Category_Refinery%20Gases_December_2011.pdf