SCREENING-LEVEL HAZARD CHARACTERIZATION

Crude Butadiene C4 Category

SPONSORED CHEMICALS
(See Table 1)

SUPPORTING CHEMICALS

1,3-Butadiene	**CASRN 106-99-0**
Ethylene	**CASRN 74-85-1**
Pentane	**CASRN 109-66-0**
2-Butene, 2-methyl-	**CASRN 513-35-9**

The High Production Volume (HPV) Challenge Program[1] was conceived as a voluntary initiative aimed at developing and making publicly available screening-level health and environmental effects information on chemicals manufactured in or imported into the United States in quantities greater than one million pounds per year. In the Challenge Program, producers and importers of HPV chemicals voluntarily sponsored chemicals; sponsorship entailed the identification and initial assessment of the adequacy of existing toxicity data/information, conducting new testing if adequate data did not exist, and making both new and existing data and information available to the public. Each complete data submission contains data on 18 internationally agreed to "SIDS" (Screening Information Data Set[1,2]) endpoints that are screening-level indicators of potential hazards (toxicity) for humans or the environment.

The Environmental Protection Agency's Office of Pollution Prevention and Toxics (OPPT) is evaluating the data submitted in the HPV Challenge Program on approximately 1400 sponsored chemicals by developing hazard characterizations (HCs). These HCs consist of an evaluation of the quality and completeness of the data set provided in the Challenge Program submissions. They are not intended to be definitive statements regarding the possibility of unreasonable risk of injury to health or the environment.

The evaluation is performed according to established EPA guidance[2,3] and is based primarily on hazard data provided by sponsors; however, in preparing the hazard characterization, EPA considered its own comments and public comments on the original submission as well as the sponsor's responses to comments and revisions made to the submission. In order to determine whether any new hazard information was developed since the time of the HPV submission, a search of the following databases was made from one year prior to the date of the HPV Challenge submission to the present: (ChemID to locate available data sources including Medline/PubMed, Toxline, HSDB, IRIS, NTP, ATSDR, IARC, EXTOXNET, EPA SRS, etc.), STN/CAS online databases (Registry file for locators, ChemAbs for toxicology data, RTECS, Merck, etc.) and Science Direct. OPPT's focus on these specific sources is based on their being

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[1] U.S. EPA. High Production Volume (HPV) Challenge Program; http://www.epa.gov/chemrtk/index.htm.
[2] U.S. EPA. HPV Challenge Program – Information Sources; http://www.epa.gov/chemrtk/pubs/general/guidocs.htm.
[3] U.S. EPA. Risk Assessment Guidelines; http://cfpub.epa.gov/ncea/raf/rafguid.cfm.

of high quality, highly relevant to hazard characterization, and publicly available.

OPPT does not develop HCs for those HPV chemicals which have already been assessed internationally through the HPV program of the Organization for Economic Cooperation and Development (OECD) and for which Screening Initial Data Set (SIDS) Initial Assessment Reports (SIAR) and SIDS Initial Assessment Profiles (SIAP) are available. These documents are presented in an international forum that involves review and endorsement by governmental authorities around the world. OPPT is an active participant in these meetings and accepts these documents as reliable screening-level hazard assessments.

These hazard characterizations are technical documents intended to inform subsequent decisions and actions by OPPT. Accordingly, the documents are not written with the goal of informing the general public. However, they do provide a vehicle for public access to a concise assessment of the raw technical data on HPV chemicals and provide information previously not readily available to the public.

Category Name	Crude Butadiene C4 Category
Chemical Abstract Service Registry Number (CASRN)	**Sponsored Chemicals** **See Table 1** **Supporting Chemicals** **106-99-0** **74-85-1** **109-66-0** **513-35-9**
Chemical Abstract Index Name	**Sponsored Chemicals** **See Table 1** **Supporting Chemicals** **1,3-Butadiene** **Ethene** **Pentane** **2-Butene, 2-methyl-**
Structural Formula	**Sponsored Chemicals** **See representative structures in Appendix** **Supporting Chemicals** **See representative structures in Appendix**

Summary

The crude butadiene C4 category consists of two process streams (C4 crude butadiene stream and the butadiene unit heavy ends stream) which arise from the production processes associated with ethylene manufacturing. The substances of this category are gasses possessing high vapor pressure and moderate water solubility. All category members are expected to possess high mobility in soil. Volatilization is expected to be high. The rate of hydrolysis is expected to be negligible. The rate of atmospheric photooxidation is expected to be slow to rapid for the members of this category. The members of the crude butadiene C4 category are expected to possess low persistence (P1) and low bioaccumulation potential (B1).

Since the category substances are gases, the major route of exposure to humans is via inhalation. Therefore all human health endpoints have been evaluated using the inhalation route of exposure.

The acute toxicity of the crude butadiene C4 category members in rats is low via inhalation based on a study on CASRN 68955-28-2, a stream component (containing ~45% 1,3-butadiene) and limited information on the supporting chemical, CASRN 106-99-0. CASRN 68955-28-2 is not irritating to rabbit skin or eyes.

The NOAEC for repeated-exposure inhalation toxicity of CASRN 68476-52-8, a stream component (containing ~10% 1,3-butadiene), in rats is 20 mg/L/day when administered as vapor in the combined repeated-exposure/reproductive/developmental toxicity screening test. Repeated exposure of CASRN 68955-28-2 gas for 9 days established a NOAEC of 11,140 ppm

(highest concentration tested) in rats. In the 13-week inhalation exposure study of the supporting chemical, CASRN 106-99-0, administered as gas in rats, the NOAEC was 8000 ppm (highest concentration tested). In mice, the exposure of the supporting chemical, CASRN 106-99-0, administered as gas, caused mortalities at and above 1250 ppm; the NOAEC is 625 ppm. In a 60-61 week carcinogenicity study with the supporting chemical ,CASRN 106-99-0 administered as a gas, mice showed nonneoplastic changes at 625 ppm and above.

No effects on reproductive parameters were noted in a combined repeated-exposure/reproductive/developmental toxicity screening test for CASRN 68476-52-8 vapor in rats via inhalation; the NOAEC is 20 mg/L/day (highest concentration tested). The sperm head morphology assay in mice for the supporting chemical, CASRN 106-99-0 (administered as gas), showed concentration-related increases in the percentage of abnormal sperm heads following five days of inhalation exposure to gas at concentrations of 200 to 5000 ppm. A 5-day inhalation exposure to CASRN 106-99-0, supporting chemical (gas), to male mice (mated with untreated females) in the dominant lethal test caused increases in the number of dead implantations (early) at concentrations as low as 200 ppm; although a strict concentration-response relationship was not observed. In the longer-term (4-weeks) dominant lethal test, inhalation exposure of CASRN 106-99-0, supporting chemical (gas) to male mice (mated with untreated female mice) showed early deaths at 65 ppm; the NOAEC is 12.5 ppm.

The sponsored stream component, CASRN 68476-52-8, did not show maternal or developmental toxicity in rats when administered as vapor in the combined repeated-exposure/reproductive/developmental toxicity screening test; the NOAEC was 20 mg/L/day (highest concentration tested). In the prenatal developmental toxicity study in mice via inhalation, the supporting chemical, CASRN 106-99-0 (gas) showed decreased maternal body weight gains and decreased fetal and placental weights with an increased incidence of fetal variations at 200 ppm; the NOAEC for maternal and developmental toxicity is 40 ppm. Rats showed maternal (decreased body weight gain) and developmental toxicity (fetal growth retardation) when exposed to the supporting chemical, CASRN 106-99-0 (gas) via inhalation at and above 200 ppm; the NOAEC is not established.

The sponsored stream component, CASRN 68955-28-2, was mutagenic in mammalian cells but was not mutagenic in bacteria *in vitro*, induced chromosomal aberrations *in vivo* and induced unscheduled DNA synthesis *in vitro*. The sponsored stream component, CASRN 68476-52-8, induced chromosomal aberrations *in vivo*. The supporting chemical, CASRN 106-99-0, was mutagenic in bacteria *in vitro* and induced chromosomal aberrations *in vivo*. The supporting chemical, CASRN 106-99-0, increased incidences of various tumors at multiple sites in rats and mice and there is "sufficient evidence" from epidemiologic studies of exposed workers to consider CASRN 106-99-0 carcinogenic to humans.

Based on the supporting chemicals, the 96-h LC_{50} for fish is 4.26 mg/L (CASRN 109-66-0), the 48-h EC_{50} for aquatic invertebrates is 2.7 mg/L (CASRN 109-66-0), and the 72-h EC_{50} for aquatic plants ranges from 7.5 (CASRN 109-66-0) to 40 mg/L (CASRN 74-85-1) for biomass and 10.7 (CASRN 109-66-0) to 72 mg/L (CASRN 74-85-1) for growth rate.

No data gaps were identified under the HPV Challenge Program.

The sponsor, ACC Olefins Panel, submitted a Test Plan and Robust Summaries to EPA for the Crude Butadiene C4 category on May 4, 2000. EPA posted the submission on the ChemRTK HPV Challenge website on May 19, 2000 (http://www.epa.gov/oppt/chemrtk/pubs/summaries/olefins/c12064tc.htm). EPA comments on the original submission were posted to the website on September 13, 2000. The sponsor submitted updated/revised documents on August 1, 2002, October 14, 2003, May 4, 2004 and May 17, 2005, which were posted to the ChemRTK website on August 20, 2002, December 1, 2003, August 26, 2004 and June 10, 2005, respectively.

Category Identification/Justification

Crude Butadiene C4 Category Production Streams with CASRNs and names are presented in Table 1.

The Crude Butadiene C4 Category streams arise from production processes associated with ethylene manufacturing (see Appendix for a description of the ethylene and associated processes—as presented in the test plan). In its original test plan, the sponsor grouped four production streams associated with ethylene manufacturing with 11 CASRNs into the crude butadiene C4 category. In its revised test plans, however, the sponsor separated them into two categories with two streams each: (1) crude butadiene C4 streams category and (2) pyrolysis C3+ and pyrolysis C4+ streams category. This hazard characterization pertains to the crude C4 butadiene category. A separate hazard characterization has been prepared for the pyrolysis C3+ and pyrolysis C4+ category.

The revised crude butadiene C4 category contains two streams encompassing 10 CASRNs, (1) C4 crude butadiene stream and (2) butadiene unit heavy ends stream. The C4 crude butadiene stream is produced from the distillation of a liquefied portion cracked gas. This stream typically contains hydrocarbons that are predominately C4 of which approximately 40 to 60% is 1,3-butadiene (Table 2). However, it can contain as little as 10% or as much as 82% 1,3-butadiene. The second stream, butadiene unit heavy ends, is produced from extractive distillation and contains approximately 13 to 92% 1,3-butadiene (Table 2). Other hydrocarbons in this stream are predominately C4.

These two commercial production streams are included in one category because they are similar from a process and toxicology perspective. The typical carbon (C) number distribution for these streams ranges predominantly between C3 and C5. Each stream can vary in composition, not only between manufacturers but also for an individual manufacturer, depending on feedstock type and process operating conditions. Although the chemical composition of the streams can vary, the defining characteristic of the two streams is that each contains a mixture of chemicals from a reaction or separation activity in the Olefins Industry hydrocarbon processes and each contains 1,3-butadiene at a minimum concentration of approximately 10%. 1,3-Butadiene is the most biologically active constituent and the major contributor to toxicological activity for these streams. This commonality was the basis for considering the two streams as a category for purposes of the HPV Program.

Please note: The TSCA Chemical Substance Inventory definitions for the CASRNs (see Appendix) in this category can be vague with respect to composition. Therefore, it is not uncommon that a CASRN is correctly used to describe different streams (different compositions) or that two or more CASRNs are used to describe one stream (similar composition or process). For this reason, the data matrix for this category are developed based on two compositionally differentiated process streams, rather than on the CASRNs in this category.

Table 1. Crude Butadiene C4 Category Production Streams—CASRNs and Names

Streams	CASRN	Name
C4 Crude Butadiene	68476-52-8	Hydrocarbons, C4, Ethylene-Manuf.-By-Product
	68187-60-0	Hydrocarbons, C4, Ethane-Propane-Cracked
	68955-28-2	Gases, (Petroleum), Light Steam-Cracked, Butadiene Conc.
	64742-83-2	Naphtha, (Petroleum), Light Steam Cracked
	68476-44-8	Hydrocarbons, >C3
	68956-54-7	Hydrocarbons, C4, Unsaturatedd.
	68477-41-8	Gases, Petroleum, Extractive, C3-5, Butadiene-Butene-Rich
	25167-67-3	Butene
Butadiene Unit Heavy Ends	69103-05-5	Hydrocarbons, C4-7, Butadiene Manuf. By-Product
	68477-41-8	Gases, Petroleum, Extractive, C3-5, Butadiene-Butene-Rich
	68512-91-4	Hydrocarbons, C3-4-Rich, Petroleum Distillates

Supporting Chemicals Justification

For the purposes of hazard characterization, 1,3-butadiene is used to address human health effects endpoints because as stated above, the major stream in the category on a production volume basis is a C4 stream that contains between approximately 10 to 82% 1,3-butadiene. Both streams contain significant levels of 1,3-butadiene which is the most biologically active constituent and the major contributor to toxicological activity. 1,3-Butadiene has been assessed at SIAM 4 under the OECD HPV Program; http://ecb.jrc.ec.europa.eu/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/butadienereport019.pdf. An EPA IRIS assessment is also available for 1,3-butadiene (CASRN 106-99-0: http://www.epa.gov/ncea/iris/subst/0139.htm).

For aquatic toxicity, the sponsor indicated that measured data on aquatic toxicity endpoints are not available for the category streams, and instead submitted ECOSAR estimations for six constituents of the streams (isobutane, n-butane, isobutylene, cis- and trans-butene-2, butane-1 and 1,3-butadiene). However, EPA determined that the measured data from ethylene (CASRN 74-85-1), pentane (CASRN 109-66-0) and 2-butene, 2-methyl- (CASRN 513-35-9) are more appropriate than estimated ECOSAR values to support this category based on their similar physico-chemical properties, environmental fate characteristics and mode of toxic action (narcosis). In addition, these chemicals are used to set boundaries for the category streams covering the low and high carbon numbers for the category members (C3-C5). Therefore, data from these supporting chemicals are considered adequate for characterizing the aquatic toxicity hazard for this category CASRNs 74-85-1, 109-66-0 and 513-35-9 have been assessed at OECD SIAMs under the OECD HPV program—ethylene (SIAM 5; http://www.chem.unep.ch/irptc/sids/OECDSIDS/74851.pdf); pentane (SIAM 13; http://ecb.jrc.it/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/n-pentanereport043.pdf)) and 2-butene, 2-methyl-(SIAM 19; http://www.chem.unep.ch/irptc/sids/OECDSIDS/513359.pdf).

Table 2. Typical Constituent (wt%) Range in Streams of the Crude Butadiene C4 Category (as presented in the sponsor's teest plan)		
Constituent	**C4 Crude Butadiene Stream (wt %)**	**Butadiene Unit Heavy Ends Stream (wt %)**
tert-Butyl Catechol	0 - 0.01	
Methanol	0.0 - 0.3	
Methylacetylene & Propadiene	0.0 - 2.3	
Ethyl- & Vinylacetylene	0.7 - 3.0	
Propylene	0.0 - 1.9	
Other C3 & Lighter Hydrocarbons	0.5 - 1.7	
Isobutane	0.4 - 22	
Isobutylene	0.5 - 29	
n-Butane	1.5 - 30	0.0 - 6.0
cis- & trans -Butene-2	3.5 - 54	5 - 50
Butene-1	2.5 - 25	0.0 - 4.0
1,3-Butadiene	10 - 82	13 - 92
1,2-Butadiene	0.0 - 1.4	0.0 - 2.0
Other C5 & Higher	0.0 - 8.0	
Vinylcyclohexene	0.0 - 1.0	
Isopentane	0.0 - 3.0	0.0 – 3.0
Other C8 Hydrocarbons	0.0 - 4.0	0.0 – 4.0

Note 1: The balance of these streams is expected to be other hydrocarbons that have boiling points in the ranges of the listed constituents.
Note 2: The ranges should not be considered to represent absolute limits for these streams. They represent the high and low reported values, and are industry typical limit values.

1. Chemical Identity

1.1 Identification and Purity

Some human health endpoints were tested on the following streams for which the robust summaries provided the following composition:

(1) CASRN 68476-52-8, C4 crude butadiene with low 1,3-butatdiene content (~10% 1,3-butadiene, 4% isobutene, 4% n-butane, 29% *trans*-2-butene, 29% 1-butnene, 11% isobutylene and 12% *cis*-2-butene). This stream is representative of CASRNs 25167-67-3, 64742-83-2, 68187-60-0, 68476-44-8, 68955-28-2 and 68954-7.

(2) CASRN 68955-28-2, Gases (petroleum) light steam-cracked, butadiene conc. (~45% 1,3-butadiene, 20% butanes and 30% butenes)

(3) CASRN 68955-28-2, Gases (petroleum) light steam-cracked, butadiene conc. (~67% 1,3-butadiene, 30% butanes, and 2% 1,2-butaidene)

In addition, in robust summaries the purity of 1,3-butadiene (supporting chemical for human health endpoints) is reported to be > 98.94%.

1.2 Physical-Chemical Properties

The physical-chemical properties of the sponsored substances contained in the crude butadiene C4 category and its supporting chemicals are summarized in Table 3. A description of the complex mixtures used for this category and the chemical structures of the specific compounds is provided in Appendix A.

The components of this category are gasses that possess high vapor pressure and moderate water solubility.

Table 3. Physical-Chemical Properties of the Crude Butadiene C4 Category[1]

Property	C4 Crude Butadiene Stream[2]	Butadiene Unit Heavy Ends Stream[3]	1,3-Butadiene (Supporting Chemical)
CASRN	68476-52-8; 68187-60-0; 68955-28-2; 64742-83-2; 68476-44-8; 68956-54-7; 68477-41-8; 25167-67-3	106-99-0; 69103-05-5; 68477-41-8; 68512-91-4	106-99-0
Molecular Weight	Complex mixture	Complex mixture	54.09
Physical State	Gas	Gas	Gas
Melting Point (°C)	-185.3 to -105.5 (measured)[4]	-138.9 to -105.5 (measured)[4]	-108.9 (measured)[4]
Boiling Point (°C)	-11.7 to 3.7 (measured)[4]	-4.4 to 3.7 (measured)[4]	-4.4°C (measured)[4]
Vapor Pressure (mm Hg at 25°C)	1,600 to 2,610 (measured)[4]	1,600 to 2,110 (measured)[4]	2,110 (measured)[4]
Dissociation Constant (pK_a)	Not applicable		
Henry's Law Constant (atm-m^3/mol)	0.074 to 1.19 (measured)[4]	0.074 to 0.231 (measured)[4]	0.074 (measured)[4]
Water Solubility (mg/L at 25°C)	48.8 to 735 (measured)[4]	511 to 735 (measured)[4]	735 (measured)[4]

Table 3. Physical-Chemical Properties of the Crude Butadiene C4 Category[1]			
Property	**C4 Crude Butadiene Stream[2]**	**Butadiene Unit Heavy Ends Stream[3]**	**1,3-Butadiene (Supporting Chemical)**
Log K_{ow}	1.99 to 2.89 (measured)[4]	1.99 to 2.33 (measured)[4]	1.99 (measured)[4]

[1] Chemicals Manufacturing Association Olefins Panel, HPV Implementation Task Group. May 5, 2004. Revised Test Plan and Robust Summary for the Crude Butadiene C4 Category. Available online from: http://www.epa.gov/chemrtk/pubs/summaries/olefins/c12064tc.htm as of August 18, 2010.
[2] Based on the chemical composition of this process stream (see Appendix A) data was derived from: propane, 2-methyl- (75-28-5); butane (106-97-8); 1-propene, 2-methyl- (115-11-7); 2-butene, (2Z)- (590-18-1); 2-butene, (2E)- (624-16-6); 1-butene (106-98-9); and 1,3-butadiene (106-99-0).
[3] Based on the chemical composition of this process stream (see Appendix A) data was derived from 2-butene, (2Z)- (590-18-1); 2-butene, (2E)- (624-16-6); and 1,3-butadiene (106-99-0).
[4] SRC. The Physical Properties Database (PHYSPROP). SRC, Inc., Syracuse, NY. Available online from: http://www.syrres.com/esc/physprop.htm as of August 18, 2010.

2. General Information on Exposure

2.1 Production Volume and Use Pattern

The crude C4 butadiene category chemicals had an aggregated production and/or import volume in the United States greater than seven billion 760 million pounds in calendar year 2005.

- CASRN 64742-83-2: 1 billion pounds and greater;
- CASRN 68187-60-0: 100 to <500 million pounds;
- CASRN 68476-44-8: 50 to <100 million pounds;
- CASRN 68476-52-8: 1 billion pounds and greater;
- CASRN 68477-41-8: 1 billion pounds and greater;;
- CASRN 68512-91-4: 500 to < 1 billion pounds;
- CASRN 68513-68-8: 100 to <500 million pounds;
- CASRN 68955-28-2: 1 billion pounds and greater;
- CASRN 68956-54-7: 1 billion pounds and greater;
- CASRN 69103-05-5: 10 to <50 million pounds;
- CASRN 25167-67-3: 1 billion pounds and greater;

CASRN 64742-83-2, 68187-60-0, 68476-44-8, 68477-41-8, 68512-91-4, 68513-68-8, 68955-28-2 and 68956-54-7:
No industrial processing and uses and commercial and consumer uses were reported for these chemicals.

CASRN 68476-52-8:
Non-confidential information in the IUR indicated that the industrial processing and uses of the chemical include petrochemical manufacturing as intermediates. Non-confidential commercial and consumer uses of this chemical include rubber and plastic products.

CASRN 69103-05-5:
Industrial processing and uses are claimed confidential. No commercial and consumer uses were reported for this chemical.

CASRN 25167-67-3:
Non-confidential information in the IUR indicated that the industrial processing and uses of the chemical include petroleum refineries as intermediates. Commercial and consumer uses include lubricants, greases and fuel additives.

2.2 Environmental Exposure and Fate

The components of the crude butadiene C4 category are expected to possess high mobility in soil. 1,3-Butadiene and supporting chemical, 1-butene, were not readily biodegradable, achieving less than 5% biodegradation within 28 days in a closed bottle test (OECD 301D); however, several substances in this category have been shown to degrade using mixed microbial or pure cultures isolated from various sources. Propane, 2-methyl- achieved 49% mineralization in 20 days following a 6 day lag period and using the mixed microbial cultures isolated from municipal sewage sludge. Butane was completely degraded after 34 days using the same set of cultures. The half-life of 1,3-butadiene in aerobic waters has been reported as approximately 7 days and the half-life in anaerobic waters was reported as 28 days. Volatilization of these substances is expected to be high based on the Henry's Law constants of these substances. The rate of hydrolysis is expected to be negligible since the substances in this category do not possess functional groups that hydrolyze under environmental conditions. The members of the crude butadiene C4 category are expected to possess low persistence (P1) and low bioaccumulation potential (B1).

The environmental fate properties are provided in Table 4.

Table 4. Environmental Fate Properties of the Crude Butadiene C4 Category[1]

Property	C4 Crude Butadiene Stream[2]	Butadiene Unit Heavy Ends Stream[3]	1,3-Butadiene Supporting Chemical
CASRN	68476-52-8; 68187-60-0; 68955-28-2; 64742-83-2; 68476-44-8; 68956-54-7; 68477-41-8; 25167-67-3	69103-05-5; 68477-41-8; 68512-91-4	106-99-0
Photodegradation Half-life	1.9–52.6 hours (estimated)[4]	1.9–2.3 hours (estimated)[4]	1.9 hours (estimated)[4]
Hydrolysis Half-life	Stable		
Biodegradation	No data	No data	0–4% after 28 days (not readily biodegradable)[5]; Half-life 7 days in aerobic water and 28 days in anaerobic waters[6]
Bioaccumulation Factor	BAF = 10–61 (estimated)[4]	BAF = 10–21 (estimated)[4]	BAF = 10 (estimated)[4]
Log K_{oc}	1.5–1.6 (estimated)[4]	1.5–1.6 (estimated)[4]	1.6 (estimated)[4]
Fugacity (Level III Model)[4]			
Air (%)	3.0–48.4	3.0–5.7	5.7
Water (%)	50.6–94.6	90.9–94.6	90.9
Soil (%)	0.7–3.0	2.1–3.0	3.0
Sediment (%)	0.2–0.3	0.3	0.3
Persistence[7]	P1 (low)	P1 (low)	P1 (low)
Bioaccumulation[7]	B1 (low)	B1 (low)	B1 (low)

[1] Chemicals Manufacturing Association Olefins Panel, HPV Implementation Task Group. May 5, 2004. Revised Test Plan and Robust Summary for the Crude Butadiene C4 Category. Available online from: http://www.epa.gov/chemrtk/pubs/summaries/olefins/c12064tc.htm as of August 18, 2010.
[2] Based on the chemical composition of this process stream (see Appendix A) data was derived from: propane, 2-methyl- (75-28-5); butane (106-97-8); 1-propene, 2-methyl- (115-11-7); 2-butene, (2Z)- (590-18-1); 2-butene, (2E)- (624-16-6); 1-butene (106-98-9); and 1,3-butadiene (106-99-0).
[3] Based on the chemical composition of this process stream (see Appendix A) data was derived from 2-butene, (2Z)- (590-18-1); 2-butene, (2E)- (624-16-6); and 1,3-butadiene (106-99-0).
[4] U.S. EPA. 2010. Estimation Programs Interface Suite™ for Microsoft® Windows, v4.00. U.S. Environmental Protection Agency, Washington, DC, USA. Available online from: http://www.epa.gov/opptintr/exposure/pubs/episuitedl.htm as of August 18, 2010.
[5] National Institute of Technology and Evaluation. 2002. Biodegradation and Bioaccumulation of the Existing Chemical Substances under the Chemical Substances Control Law. Available online from: http://www.safe.nite.go.jp/english/kizon/KIZON_start_hazkizon.html as of August 18, 2010.
[6] Capel P., Larson S. 1995. A chemodynamic approach for estimating losses of target organic chemicals from water during sample holding time. Chemosphere 30: 1097–1107.
[7] Federal Register. 1999. Category for Persistent, Bioaccumulative, and Toxic New Chemical Substances. *Federal Register* 64, Number 213 (November 4, 1999) pp. 60194–60204.

Conclusion: The crude butadiene C4 category consists of 1,3-butadiene and two process streams (C4 crude butadiene stream and the butadiene unit heavy ends stream) which arise from the production processes associated with ethylene manufacturing. The substances of this category are gasses possessing high vapor pressure and moderate water solubility. All category members are expected to possess high mobility in soil. Volatilization is expected to be high. The rate of hydrolysis is expected to be negligible. The rate of atmospheric photooxidation is expected to be slow to rapid for the members of this category. The members of the crude butadiene C4 category are expected to possess low persistence (P1) and low bioaccumulation potential (B1)

3. Human Health Hazard

A summary of health effects data submitted for SIDS endpoints is provided in Table 5. The table also indicates where data for tested category members are read-across (RA) to untested members of the category.

Acute Inhalation Toxicity

Gases (petroleum) light steam-cracked, butadiene conc. (CASRN 68955-28-2)
Fischer 344 rats (5/sex/dose) were exposed via whole body inhalation to CASRN 68955-28-2 (approximately 45% 1,3-butadiene, 20% butanes and 30% butenes) at 5300 mg/m^3 (2331 ppm) for 4 hours and observed for 14 days. No mortalities were observed.
LC_{50} > 5.3 mg/L

1,3-Butadiene (CASRN 106-99-0, supporting chemical)
In the rat, 4-hour LC_{50} value was reported to be 285 mg/L (129,000 ppm). Information is not available on the strain, age, number and sex, number of exposure concentrations or post observation period. (http://ecb.jrc.ec.europa.eu/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/butadienereport019.pdf)
LC_{50} = 129,000 ppm

Repeated-Dose Toxicity

C4 crude butadiene (CASRN 68476-52-8, ~10% 1,3-butadiene content; representing CASRNs 25167-67-3, 64742-83-2, 68187-60-0, 68476-44-8, 68955-28-2, 68956-54-7)
In a combined repeated-dose/reproductive/developmental toxicity screening test, Sprague-Dawley rats (12/sex/concentration) were exposed to CASRN 68476-52-8 vapor (~10% 1,3-butadiene, 4% isobutane, 4% n-butane, 29% *trans*-2-butene, 29% 1-butene, 11% isobutylene and 12% *cis*-2-butene) via whole-body inhalation, at concentrations of 0, 2, 10 or 20 mg/L 6 hours/day, 7 days/week for 36 – 37 days. (Targeted exposure concentrations were not met on one entire exposure duration and during brief periods on a few other days. However, the affected instances were limited relative to the total duration of the study and did not have significant impact on study integrity.) There were no deaths and no treatment-related clinical signs were noted. No differences in body weights and food consumption were observed for the males or

females at any concentration throughout the duration of the study. Sensory evaluation, rectal temperature, fore/hind limb grip performance and motor activity data revealed no treatment-related effects. No treatment-related changes were noted for prothrombin time, hematology values or clinical chemistry measurements in males and females at any concentration. There were no effects on organ weights, gross pathology or histopathology in any of the exposed groups when compared to their respective controls.
NOAEC = 20 mg/L/day (highest concentration tested)

Gases (petroleum) light steam-cracked, butadiene conc. (CASRN 68955-28-2, ~45% 1,3-butadiene)
Fischer 344 rats (5/sex/dose) were exposed to CASRN 68955-28-2 gas (~45% 1,3-butadiene, 20% butanes and 30% butenes) via whole-body inhalation at concentrations of 0, 1110 and 11,140 ppm, 6 hours/day for 9 days. Most rats in both exposure groups appeared normal throughout the study. Nasal discharge was observed in some rats of both groups and at a greater incidence in the high-exposure group. There were no differences between the control and exposed groups for mean body weight, organ weight, hematology or blood chemistry values. There were no exposure-related histopathological changes in any of the organs or tissues examined.
NOAEC = 11,140 ppm (highest concentration tested)

1,3-Butadiene (CASRN 106-99-0, supporting chemical)
(1) Sprague-Dawley rats (40/sex/concentration) were exposed to 1,3-butadiene gas (purity > 99.2%, containing 120 ppm t-butyl catechol;) via whole-body inhalation at concentrations of 0, 1000, 2000, 4000 or 8000 ppm for 6 hours/day, 5 days/week for 13 weeks. Interim sacrifices were performed on 10 rats/sex/group after 2 and 6 weeks of exposure. Increased salivation was observed in females after 8 weeks and decreased grooming (stained fur) in the males after 10 weeks. No other exposure-related clinical signs were observed. Male rats showed slight reductions in body weight gains compared to the controls. Food consumption, blood and urine analyses, measurement of brain cholinesterase activity, organ weight measurements and histopathological examinations (high dose only) were comparable to control values.
NOAEC ~ 8000 ppm (highest concentration tested)

(2) In an NTP study, B6C3F1 mice (10/sex/dose) were exposed to 1,3-butadiene gas (rubber grade, containing 0.02% t-butyl catechol;) via whole-body inhalation at concentrations of 0, 625, 1250, 2500, 5000 or 8000 ppm for 6 hours/day, 5 days/week for 14 weeks (64 exposures). Because four male mice in the high-exposure group died by day 4, another two groups of 10 male mice each were restarted (control and 8000 ppm). At the end of the 95- or 93-day (restart) studies, surviving mice were sacrificed. Histopathologic examination was conducted on animals from the control and high-dose groups. Mortalities and/or morbidities occurred at 1250 ppm and above. Body weights were decreased at 2500 ppm and above in males and at 5000 ppm and above in females. No exposure-related histopathological changes were observed. [This study was conducted at IBT.]
LOAEC ~ 1250 ppm (based on mortalities)
NOAEC ~ 625 ppm

(3) In an NTP carcinogenicity study, B6C3F1 mice (50/sex/concentration) were exposed to

1,3-butadiene gas via whole-body inhalation at concentrations of 0, 625 or 1250 ppm, 6 hours/day, 5 days/week for 60 – 61 weeks. Survival was markedly reduced in exposed animals due primarily to the development of malignant tumors. Histopathological examination was conducted. A wide range of organs was affected by exposure to butadiene (see also under carcinogenicity). Non-neoplastic changes at 625 and 1250 ppm included ovarian and testicular atrophy, congestion, hemorrhage and hyperplasia of the lungs, hemorrhage and necrosis of the liver, thymus and bone marrow atrophy, epithelial hyperplasia of the forestomach and endothelial hyperplasia and mineralization of the heart. Chronic inflammation and fibrosis developed in the nasal cavities of males exposed to 1250 ppm. 1,3-Butadiene caused severe toxicity in mice at these concentrations. (http://ntp-apps.niehs.nih.gov/ntp_tox/index.cfm?fuseaction=ntpsearch.searchhome)

Reproductive Toxicity

C4 crude butadiene (low 1,3-butadiene content) (Primary CASRN 68476-52-8)
In the combined repeated-dose/reproductive/developmental toxicity screening test in rats described above, the study design included a main study for repeated-dose toxicity endpoints and a reproductive/developmental toxicity satellite groups (12 females/dose) that were exposed to CASRN 68476-52-8 vapor via inhalation at concentrations of 0, 2, 10 or 20 mg/L, for 6 hours/day, 7 days/week for 2 weeks prior to mating, during mating (up to 2 weeks) and continuing through day 19 of gestation. (Males from the main study were used to breed these females.) Males (from the main study) were exposed for 36 – 37 days. The dams were allowed to deliver their litters, which were retained until postnatal day 4. There were no deaths and no treatment-related clinical observations were noted. No differences in parental body weights, body weight gains or feed consumption were observed at any dose level throughout the duration of the study. There were no treatment-related effects on any reproductive parameters including measures of reproductive performance (mating, conception and fertility, time to mating, gestation length, and litter size) or offspring survival (gestation and postnatal survival indices, percent pre- and post-implantation loss).
NOAEC (systemic/reproductive toxicity) = 20 mg/L/day (highest concentration tested)

1,3-Butadiene (CASRN 106-99-0, supporting chemical)
(1) A recent (2002) Integrated Risk Information System (IRIS) review by EPA on 1,3-butadiene is available at http://www.epa.gov/ncea/iris/subst/0139.htm.

The most sensitive reproductive endpoint observed in subchronic studies with CASRN 106-99-0 was fetal deaths in dominant lethal studies in mice exposed for 28-days at 65 ppm (see *Other* section for details); the NOAEC was 12.5 ppm. In two-year bioassays, the most sensitive reproductive effects were ovarian atrophy in female mice at 6.25 ppm and testicular atrophy in male mice at 625 ppm. The NOAEC for reproductive toxicity in female mice was not established and in male mice was 200 ppm (see *Carcinogenicity* section for details).

(2) In a combined reproductive/developmental toxicity screening test (OECD TG 421), Sprague-Dawley rats (12/sex/concentration) were exposed whole-body to 1,3-butadiene as a vapor at 0, 300, 1500 or 6000 ppm (approximately 0, 0.66, 3.3 or 13.3 mg/L) for 6 hours/day. Animals of both sexes were exposed for 2 weeks prior to mating and 2 weeks during mating. Males

continued to be exposed after mating for a total of 70 days. Females were exposed on gestation days 0 – 19 and postnatal days 5 – 18. After weaning on postnatal day 21, one male and one female from each litter were exposed for 7 days to the same concentration of 1,3-butadiene as its dam. Beginning on postnatal day 28, previously unexposed weanlings (1/sex/litter) were exposed for 7 days to the same concentration of 1,3-butadiene as their dams. Reproductive endpoints included assessments of gonadal function, mating behavior, conception, gestation and parturition (details not specified). Reductions in body weight parameters (details not specified) were observed in the parental generation and offspring at concentrations ≥ 3.3 mg/L. Transient reductions in food consumption were observed in the parental generation during the first week of exposure. Clinical signs at 13.3 mg/L included chromodacryorrhea, chromorhinorrhea and salivation in the parental generation and infrequent occurrences of dried red material in the perioral and perinasal regions of four exposed pups. No reproductive effects were observed. (HPV Challenge submission for Petroleum Hydrocarbon Gases Category: http://www.epa.gov/hpv/pubs/summaries/ptrlgas/c13224tc.htm)
NOAEC (reproductive toxicity) ~ 13.3 mg/L/day (highest concentration tested)

(3) See human health data at http://ecb.jrc.ec.europa.eu/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/butadienereport019.pdf.

Developmental Toxicity

C4 crude butadiene (low 1,3-butadiene content) (Primary CASRN 68476-52-8)
In the combined repeated-dose/reproductive/developmental toxicity screening test in Sprague-Dawley rats described above, additional reproductive/developmental toxicity satellite groups (12 females/dose) were exposed to the C4 crude butadiene vapor (~10% 1,3-butadiene, 4% isobutene, 4% n-butane, 29% *trans*-2-butene 29% 1-butene, 11% isobutylene and 12% *cis*-2-butene) via inhalation at concentrations of 0, 2, 10 or 20 mg/L, for 6 hours/day, 7 days/week for 2 weeks prior to mating, during mating (up to 2 weeks) and continuing through day 19 of gestation. The dams were allowed to deliver their litters, which were retained until postnatal day 4. There were no deaths or treatment-related clinical observations noted. No differences in parental body weights, body weight gains or feed consumption were observed at any dose level tested throughout the duration of the study. There were no treatment-related effects on any developmental parameters including offspring survival, gestation and postnatal survival indices, percent pre- and post-implantation loss or grossly visible abnormalities.
NOAEC (maternal/developmental toxicity) = 20 mg/L/day (highest concentration tested)

1,3-Butadiene (CASRN 106-99-0, supporting chemical)
(1) CD-1 Swiss mice (18 – 22 pregnant females/concentration) were exposed to 1,3-butadiene gas (purity 99.88%) via inhalation at concentrations of 0, 40, 200 or 1000 ppm for 6 hours/day on days 6 – 15 of gestation. There were decreases in maternal body weight gains at 200 (14%) and 1000 ppm (20%). Fetal weights were reduced in both males and females at 200 (16% less than control_ and 1000 ppm (22% less than control) ; placenta weights were reduced for corresponding male fetuses at 200 ppm and both males and females at 1000 ppm. There were no significant differences in percent resorptions or malformations per litter, although there was an increase in fetal variations (supernumary ribs and reduced ossification of sternebrae) at the two

highest concentrations. A slight but statistically significant decrease in male fetal weight (95% of control) was seen at 40 ppm.
LOAEC (maternal and developmental toxicity) ~ 200 ppm (based on decreased maternal body weight gains, decreased fetal and placental weights and increased incidence of fetal variations)
NOAEC (maternal and developmental toxicity) ~ 40 ppm

(2) In an NTP study, Sprague-Dawley rats (24 – 28 pregnant females/dose) were exposed to 1,3-butadiene gas (purity 99.88%) via inhalation at doses of 0, 40, 200 or 1000 ppm 6 hours/day on days 6 – 15 of gestation. The only effect observed was decreased body weight gains in the dams at 1000 ppm. The percentage of pregnant animals and number of litters with live fetuses were unaffected by treatment. There were no differences among the groups for number of live fetuses per litter, percent resorptions or malformations per litter, placental or fetal body weights or sex ratio. There was no evidence of developmental toxicity or adverse reproductive effects in any of the exposed groups.
LOAEC (maternal toxicity) ~ 1000 ppm (based on decreased maternal body weight gains)
NOAEC (maternal toxicity) ~ 200 ppm
NOAEC (developmental toxicity) ~ 1000 ppm (highest concentration tested)

(3) Pregnant Sprague-Dawley rats (40 in control group, 24/concentration in treatment groups and 26 in a positive control group) were exposed to 1,3-butadiene gas via inhalation at concentrations of 0, 200, 1000 or 8000 ppm for 6 hours/day from day 6 to 15 of gestation and sacrificed on day 20. No treatment-related mortalities or clinical signs were observed. There was a dose-related decrease in maternal body weights and body weight gains at all concentrations. There was no effect on pregnancy rate, implantation or pre-implantation loss or gravid uterus weight. Post-implantation loss was slightly higher (but not statistically significant) at all concentrations than in the control group. Mean fetal weight and crown/rump length were lower than the control group at all concentrations; statistically significant at 8000 ppm. Fetal sex ratio was unaffected. There was a higher incidence of minor fetal defects and variants, a decrease in fetal growth rates at all dose levels and an increase in the incidence of major fetal defects (wavy ribs) at 8000 ppm. Overall, there was dose-related embryonic growth retardation at all concentrations. Study details are from TSCATS (OTS0505459).
LOAEC (maternal/developmental toxicity) = 200 ppm (based on decreased maternal body weight gains and fetal growth retardation, respectively)
NOAEC (maternal/developmental toxicity) = Not established

(4) In the combined inhalation reproductive/developmental toxicity screening test in Sprague-Dawley rats described previously, developmental endpoints included assessments of conception, parturition, lactation and development of offspring (details not specified). No developmental effects were observed.
LOAEC (maternal toxicity) = 3.3 mg/L (based on reductions in body weight parameters)
NOAEC (maternal toxicity) = 0.66 mg/L
NOAEC (developmental toxicity) = 13.3 mg/L (highest concentration tested)

(5) See human health data at http://ecb.jrc.ec.europa.eu/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/butadienereport019.pdf.

Genetic Toxicity – Gene Mutation

In vitro

Gases (petroleum) light steam-cracked, butadiene conc. (CASRN 68955-28-2)

(1) *Salmonella* strains TA98, TA100, TA1535, TA1537, TA1538 were exposed to gases (petroleum) light steam-cracked, butadiene conc. (~67% 1,3-butadiene, 30% butanes and 2% 1,2-butadiene) with and without metabolic activation at concentrations of 25, 50, 75 or 100 µL/plate. Both positive and negative controls were run; however, their responses were not reported. Cytotoxicity was noted at > 75 µL in TA 100 and > 100 µL in TA1537 in the preliminary assay. Some inconsistencies in toxicity with increasing dose level were noted that were attributed to the volatility of the test substance. None of the five strains exhibited reversion frequencies substantially different from controls.

Gases (petroleum) light steam-cracked, butadiene conc. was not mutagenic in this assay.

(2) Mouse lymphoma cells ((L5178Y) were exposed to gases (petroleum) light steam-cracked, butadiene conc. (~67% 1,3-butadiene, 30% butanes and 2% 1,2-butadiene) at concentrations of 10, 12.5, 15, 17.5, 20, 22.5, 25, 27.5, 30, 35, 40 or 45 µL/mL without metabolic activation and 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, 22.5 or 25 µL/mL with metabolic activation. Both positive and negative controls were run. Positive control responses were not reported. Without metabolic activation, mutant frequencies and total number of mutants were increased at 20.0 and 22.5 µL/mL. Cytotoxic concentration was not reported. There were no differences in mutant frequency for the S9 activated cultures.

Gases (petroleum) light steam-cracked, butadiene conc. was mutagenic in the absence of metabolic activation in this assay.

1,3-Butadiene (CASRN 106-99-0, supporting chemical)

(1) *Salmonella* strains TA97, TA98, TA100, TA1535 were exposed to 1,3-Butadiene at concentrations of 0, 30, 40, 50 and 60% in air, with and without rat, mouse or human liver S9 metabolic activation systems. Both positive and negative controls were run and they responded appropriately. 1,3-Butadiene induced revertants only in strain TA1535. At 30%, slightly higher activity was noted using the mouse liver S9 activation system than the rat or human S9 activation system. At concentrations > 30%, the number of revertants decreased in the presence of rat or human S9. Results from the human S9-activated treatments did not differ substantially from those of the non-activated treatment. The results were similar for rat liver S9 activation system and uninduced mouse liver S9 activation system. Increasing the concentration of rat S9 (from 0.8 to 4.0 mg/plate) had no effect on the number of revertants. Positive control responded appropriately. Cytotoxic concentration was not reported.

1,3-Butadiene was mutagenic in this assay.

(2) See human health data at http://ecb.jrc.ec.europa.eu/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/butadienereport019.pdf.

Genetic Toxicity – Chromosomal Aberrations

In vivo

C4 crude butadiene (10% 1,3-butadiene conten, CASRN 68476-52-8)

In a mammalian erythrocyte micronucleus assay, B6C3F1 mice (6/sex/dose) were exposed to C4 crude butadiene (low 1,3-butadiene content; approximately 10% 1,3-butadiene, 4% isobutane, 4% n-butane, 29% *trans*-2-butene, 29% 1-butene, 11% isobutylene and 12% *cis*-2-butene) at concentrations of 0, 0.5, 10 and 20 mg/L via whole-body inhalation for 4 hours/day for 2 days. Twenty four hours after the second treatment, bone marrow was collected and smears were prepared. Statistically significant increases in the frequencies of micronucleated polychromatic erythrocytes were seen (MN-PCE) in both sexes of all treated groups compared to the negative controls. The positive control responded appropriately.
C4 crude butadiene (low 1,3-butadiene content) induced chromosomal aberrations in this assay.

Gases (petroleum) light steam-cracked, butadiene conc. (CASRN 68955-28-2)

In a mammalian erythrocyte micronucleus assay, Crl:CD-1 BR Swiss mice (10/sex/dose) were exposed to gases (petroleum) light steam-cracked, butadiene conc. (~ 45% 1,3-butadiene, 20% butanes and 30% butenes) at concentrations of 10,780, 20,671 or 35,430 ppm via whole-body inhalation, 2 hours/day for 2 days. Following the exposure, five mice/sex/group were sacrificed on days 3 and 4 and bone marrow smears were prepared. Positive control animals (5/sex) were sacrificed on day 3 only. No mice died during the study; the only clinical observation was an apparent unconsciousness during exposure. There were no body weight differences. Mice in the exposed groups showed increased micronuclei formation at all levels in both sexes. There was no change in the polychromatic/normochromatic erythrocytes (PCE/NCE) ratio in any group. The negative and positive control groups produced appropriate responses.
Gases (petroleum) light steam-cracked, butadiene conc. induced chromosomal aberrations in this assay.

1,3-Butadiene (CASRN 106-99-0, supporting chemical)

(1) In a mammalian erythrocyte micronucleus assay, Wistar rats (10 males/dose) and CB6F1 mice (20 females/dose) were exposed to 1,3-butadiene at concentrations of 0, 50, 200 or 500 ppm via inhalation 6 hours/day for 5 days. An additional group of mice was exposed to 1300 ppm. The animals were sacrificed 1 day after the last exposure and smears of peripheral blood and bone marrow erythrocytes were prepared. In rats no effects on micronuclei frequency were seen in the peripheral blood or bone marrow at all exposure concentrations. In mice, 1,3-butadiene induced micronuclei in peripheral blood and bone marrow erythrocytes at ≥50 ppm.
1,3-Butadiene induced chromosomal aberrations in mouse erythrocytes in this assay.

(2) In a mammalian erythrocyte micronucleus assay, Syrian hamsters (20 males) and B6C3F1 mice (20 males) were exposed to 1,3-butadiene via whole-body inhalation at concentrations of 0 (room air) or 1000 ppm, 6 hours/day for 2 consecutive days. Twenty four hours after the final exposure animals were euthanized and bone marrow slides were prepared and evaluated for micronuclei. In mice and hamsters a statistically significant ($p<0.01$) increase in micronuclei

was seen compared to controls. 1,3-Butadiene was active in inducing micronuclei in bone marrow erythrocytes. Study details are from TSCATS (OTS0524007).
1,3-Butadiene induced chromosomal aberrations in this assay.

(3) 1,3-Butadiene (> 500 ppm) was tested in male mice to assess chromosomal damage in immature male germ cells for 6 hours/day for 5 days. The mean frequency of micronucleated cells was enhanced at all exposure levels. Study details are from TSCATS (OTS0556235).
1,3-Butadiene induced chromosomal aberrations in this assay.

(4) See human health data at http://ecb.jrc.ec.europa.eu/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/butadienereport019.pdf.

Genetic Toxicity – Other

In vitro
Gases (petroleum) light steam-cracked, butadiene conc. (CASRN 68955-28-2)
In an unscheduled DNA synthesis (UDS) assay, rat primary hepatocytes were exposed to gases (petroleum) light steam-cracked, butadiene conc. (~45% 1,3-butadiene, 20% butanes and 30% butenes) at concentrations of 0, 1000, 5000, 10,000 and 20,000 ppm. Cytotoxicity was seen at and above 10,000 ppm. A weak positive response was observed for UDS at 20,000 ppm (7.74 nuclear grain counts vs. 1.24 in the air control vs. 107.13 in the positive control). A slight increase in UDS was also noted at 1000, 5000 and 10,000 ppm (4.29 – 5.14) compared to the air control. Both positive and negative controls were run and responded appropriately.
Gases (petroleum) light steam-cracked, butadiene conc. induced unscheduled DNA synthesis in this assay.

Additional Information

Skin Irritation

Gases (petroleum) light steam-cracked, butadiene conc. (CASRN 68955-28-2)
Two New Zealand White rabbits (1/sex) were administered 0.1 mL of gases (petroleum) light steam-cracked, butadiene conc. (~67% 1,3-butadiene, 30% butanes and 2% 1,2-butadiene) were administered 0.1 mL of gases (petroleum) light steam-cracked, butadiene conc. to the skin of both rabbits under occluded conditions (rubber dam). The test sites were evaluated 1, 3 and 7 days after dosing. The treated skin sites were virtually free of irritation at all observation intervals.
Gases (petroleum) light steam-cracked, butadiene conc. was not irritating to the skin of rabbits in this study.

Eye Irritation

Gases (petroleum) light steam-cracked, butadiene conc. (CASRN 68955-28-2)
Two New Zealand white rabbits (1/sex) were administered 0.1 mL of gases (petroleum) light steam-cracked, butadiene conc. (approximately 67% 1,3-butadiene, 30% butanes and 2%

1,2-butadiene) in one eye each and the untreated eye served as the control. Irritation was scored at 24, 48 and 72 hours. The eye irritation scores were 0 at all observation intervals.
Gases (petroleum) light steam-cracked, butadiene conc. was not irritating to the eyes of rabbits in this study.

Carcinogenicity

1,3 Butadiene (CASRN 106-99-0, supporting chemical)
(1) In an NTP study, B6C3F1 mice (50/sex/concentration) were exposed to 1,3-butadiene gas via inhalation at 0, 625 or 1250 ppm, 6 hours/day, 5 days/week. The study was scheduled to last 2 years but, was terminated at 60 (males) and 61 weeks (females) because of high mortality in both exposure groups. Survival was markedly reduced in exposed animals due primarily to malignant tumors. Increased incidences and early induction of hemangiosarcomas of the heart, malignant lymphomas, alveolar/bronchiolar adenomas and carcinomas, and pappilomas of the stomach in males and females were seen. In addition, in females, acinar cell carcinomas of the mammary gland, granulose cell tumors of the ovary, hepatocellular adenomas and adenomas or carcinomas (combined) were seen. 1,3-Butadiene was associated with nonneoplastic lesions in the respiratory epithelium, liver necrosis, and testicular or ovarian atrophy.
(http://ntp-apps.niehs.nih.gov/ntp_tox/index.cfm?fuseaction=ntpsearch.searchhome)
1,3-Butadiene increased incidences of various tumors at multiple sites in this assay.

(2) Sprague-Dawley rats (110/sex/concentration) were exposed to 1,3-butadiene gas via inhalation at concentrations of 0, 1000 or 8000 ppm, 6 hours/day, 5 days/week for 105 – 110 weeks. Significantly increased incidences of mammary gland tumors, Zymbal gland carcinomas, follicular cell tumors of the thyroid gland and uterine stromal carcinomas in females and increased incidences of Leydig cell tumors and pancreatic exocrine tumors in males were observed. (IISRP, 2000; See human health data at
http://ecb.jrc.ec.europa.eu/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/butadienereport019.pdf.
1,3-Butadiene increased incidences of various tumors at multiple sites in this assay.

(3) In two NTP studies, B6C3F1 mice (50 – 70/sex/dose) were exposed to 1,3-butadiene as a gas at concentrations of 6.25 – 1250 ppm for 6 hours/day, 5 days/week for up to 2 years. Treatment-related effects included increased incidences and early induction of hemangiosarcomas of the heart, malignant lymphomas, alveolar/bronchiolar carcinomas, squamous cell carcinomas of the stomach, acinar cell carcinomas of the mammary gland, malignant granulosa cell tumors of the ovary, hepatocellular adenomas and carcinomas (combined), histiocytic sarcomas and adenoacanthomas. [Details were obtained from NTP studies C50602A and C50602C. See NTP TR-434].
1.3-Butadiene was carcinogenic to mice in these studies.

(4) There is "sufficient evidence" from epidemiologic studies of exposed workers to consider 1,3-butadiene carcinogenic to humans. (http://www.epa.gov/iris/subst/0139.htm) IARC concluded that 1,3-butadiene is probably carcinogenic to humans [Group lA; (http://monographs.iarc.fr/ENG/Monographs/vol54/mono54-11.pdf)].

Other

1,3 Butadiene (CASRN 106-99-0, supporting chemical)
(1) In the sperm head morphology assay, B6C3F1 mice (20 males/concentration) were exposed to 1,3-butadiene gas (purity 99.88%) via inhalation at concentrations of 0, 200, 1000 or 5000 ppm for 6 hours/day for 5 days and observed for up to five weeks post-exposure. Mice were sacrificed during the fifth post-exposure week and examined for lesions of the reproductive tract and other gross abnormalities. Sperms were obtained from the cauda of the right epididymis, slides were prepared and examined microscopically. The morphology of at least 500 sperm heads per mouse was categorized. There was 21, 73, and 129% increase in the abnormal sperm heads at 0.44, 2.21 and 11.1 mg/L/day, respectively when compared to the controls. A statistical significance was achieved only for the values for the 1000 and 5000 ppm groups ($p < 0.05$). Since only a single time-point was examined, the effect on all stages of spermatogenesis could not be determined. Mean body weights of 1,3-butadiene-exposed groups were not significantly different from the control value. (Morrissey, R.E., et al., Environ. Health Perspect. 86, 79-84.)

(2) In a rodent dominant lethal test, CD-1 Swiss mice (20 males/dose) were exposed to 1,3-butadiene gas (purity 99.88%) via whole-body inhalation at concentrations of 0, 200, 1000 or 5000 ppm 6 hours/day for 5 consecutive days. After 5 days of exposure, the male mice were mated with unexposed females. Females were removed from cohabitation after 7 days, sacrificed 12 days later and the uterine contents examined. 1,3-Butadiene caused an increase in the percentage of females with two or more dead implants in all exposure groups in the first week following exposure. During the first week, there was a small but statistically significant increase in the number of dead implantations per pregnancy only at 1000 ppm (1.42 per pregnancy *vs* 0.78 in control). During the second week, there was a statistically significant increase in the number of dead implantations per pregnancy at 200 and 1000 ppm but not at 5000 ppm. These increases were due to increases in early deaths. No firm conclusions with regard to germ cell mutagenicity can be drawn. However, the study authors indicated that these results indicate possible adverse effects on mature cells.
LOAEC = 200 ppm (based on increased percentage of females with more than two dead implants and number of dead implantations per pregnancy)
NOAEC = Not established

(3) In a longer exposure dominant lethal test, male CD-1 mice (50/concentration) were exposed to 1,3-butadiene gas (purity >99.7%) via inhalation at concentrations of 0, 12.5, 65 or 130 ppm, 6 hours/day, 5 days/week for 4 weeks. They were then mated with unexposed females. The pregnant females were killed and examined at 17 of gestation. The uteri were examined for live/dead fetuses, early and late deaths and malformed fetuses. There were no treatment-related mortalities. Body weights, mating frequency, pregnancy rates, period of coition and number of implantation sites were not affected. There was a statistically significant increase ($p<0.01$) in early deaths per implantation per pregnancy at 65 and 130 ppm. The number of early deaths at 12.5 ppm was not increased. There was no effect on late deaths. There were two runts in two litters in controls and at 12.5 ppm; one runt at 65 ppm and 6 runts in 5 litters at 130 ppm. Macroscopic abnormalities in skeletal structure were observed at all dose levels. Skeletal examination of abnormal fetuses during the macroscopic examination showed increased

frequency of abnormalities of many parts of the skeleton in the runts from all treatment groups compared to their normal litter mates or normal controls. Mating frequency, period of coition, pregnancy rates and post-implantation loss were comparable to controls. The number of implantation sites was reduced at 65 ppm, but the impact on reproductive toxicity was unclear as there were no post-implantation losses. Study details are from TSCATS (OTS0559090).
LOAEC = 65 ppm (based on early deaths)
NOAEC = 12.5 ppm

(4) Male Sprague-Dawley rats (25/concentration) were exposed to 1,3-butadiene gas (purity >99.7%) via inhalation at concentrations of 0, 65, 400 or 1250 ppm 6 hours/day, 5 days/week for 10 weeks and then mated with untreated females. Pregnant females were sacrificed 20 days after the mating period ended. The uteri were examined for live/dead fetuses, early and late deaths and malformed fetuses. Mating frequency, period of coition, pregnancy rates and pre- or post-implantation loss were not affected by treatment. The number of implantation sites was reduced in the 65 ppm group, but the impact on reproductive toxicity was unclear as there were no post-implantation losses. All other parameters (early deaths, late deaths, including or excluding dead fetuses and fetal abnormalities) remained unchanged in all treatment groups. Study details are from TSCATS (OTS0001282).
NOAEC = 1250 ppm (highest concentration tested)

Conclusion:
The acute toxicity of the crude butadiene C4 category members in rats is low via inhalation based on a study on CASRN 68955-28-2, a stream component (containing ~45% 1,3-butadiene) and limited information on the supporting chemical, CASRN 106-99-0. CASRN 68955-28-2 is not irritating to rabbit skin or eyes.

The NOAEC for repeated-exposure inhalation toxicity of CASRN 68476-52-8, a stream component (containing ~10% 1,3-butadiene), in rats is 20 mg/L/day when administered as vapor in the combined repeated-exposure/reproductive/developmental toxicity screening test. Repeated exposure of CASRN 68955-28-2 gas for 9 days established a NOAEC of 11,140 ppm (highest concentration tested) in rats. In the 13-week inhalation exposure study of the supporting chemical, CASRN 106-99-0, administered as gas in rats, the NOAEC was 8000 ppm (highest concentration tested). In mice, the exposure of the supporting chemical, CASRN 106-99-0, administered as gas, caused mortalities at and above 1250 ppm; the NOAEC is 625 ppm. In a 60-61 week carcinogenicity study with the supporting chemical ,CASRN 106-99-0 administered as a gas, mice showed nonneoplastic changes at 625 ppm and above.

No effects on reproductive parameters were noted in a combined repeated-exposure/reproductive/developmental toxicity screening test for CASRN 68476-52-8 vapor in rats via inhalation; the NOAEC is 20 mg/L/day (highest concentration tested). The sperm head morphology assay in mice for the supporting chemical, CASRN 106-99-0 (administered as gas), showed concentration-related increases in the percentage of abnormal sperm heads following five days of inhalation exposure to gas at concentrations of 200 to 5000 ppm. A 5-day inhalation exposure to CASRN 106-99-0, supporting chemical (gas), to male mice (mated with untreated females) in the dominant lethal test caused increases in the number of dead implantations (early) at concentrations as low as 200 ppm; although a strict concentration-response relationship was not observed. In the longer-term (4-weeks) dominant lethal test, inhalation exposure of CASRN 106-99-0, supporting chemical (gas) to male mice (mated with untreated female mice) showed early deaths at 65 ppm; the NOAEC is 12.5 ppm.

Table 5. Summary of the Screening Information Data Setunder the U.S. HPV Challenge Program - Human Health Data

Endpoints	**Crude Butadiene C4 Category**		
	SPONSORED CHEMICAL C4 Crude Butadiene Stream (68476-52-8, 68187-60-0 68955-28-2, 64742-83-2 68476-44-8, 68956-54-7 68477-41-8, 25167-67-3)	**SPONSORED CHEMICAL Butadiene Unit Heavy Ends Stream (69103-05-5, 68477-41-8, 68512-91-4)**	**SUPPORTING CHEMICAL 1,3-Butadiene (106-99-0)**
Acute Inhalation Toxicity LC_{50} (mg/L)	**> 5.3[1]**	No Data > 5.3[1] (RA)	**285 (129,000 ppm)[3]**
Repeated-Dose Toxicity NOAEC/LOAEC Inhalation (ppm)	**(rat)** **NOAEC = 20 mg/L/day[2]** **(highest concentration tested)** **(rat)** **NOAEC = 11,140[1]** **(highest concentration tested)** (mouse) NOAEC ~625[3] LOAEC ~1250 (RA) (rat) NOAEC ~8000[3] (RA)	No Data (rat) NOAEC = 20 mg/L/day[2] (rat) NOAEC = 11,140[1] (mouse) NOAEC ~625[3] LOAEC ~1250 (rat) NOAEC ~8000[3] (RA)	**(mouse)** **NOAEC ~625** **LOAEC ~1250** **(rat)** **NOAEC ~8000[3]** **(highest concentration tested)**
Reproductive Toxicity NOAEC/LOAEC Inhalation (mg/L/day) **Reproductive Toxicity**	**(rat)** **NOAEC = 20 mg/L/day[2]** **(highest concentration tested)**	No Data (mouse – 28-day)[3] NOAEC = 12.5 LOAEC = 65 (mouse – 2-year)[3] NOAEC(f) = Not Established LOAEC(f) = 6.25 NOAEC(m) = 200 LOAEC (m) = 625 (rat)[3]	**(mouse – 28-day)[3]** **NOAEC = 12.5** **LOAEC = 65** **(mouse – 2-year)[3]** **NOAEC(f) = Not Established** **LOAEC(f) = 6.25** **NOAEC(m) = 200** **LOAEC (m) = 625** **(rat)[3]**

Table 5. Summary of the Screening Information Data Setunder the U.S. HPV Challenge Program - Human Health Data

Endpoints	**Crude Butadiene C4 Category**		
	SPONSORED CHEMICAL C4 Crude Butadiene Stream (68476-52-8, 68187-60-0 68955-28-2, 64742-83-2 68476-44-8, 68956-54-7 68477-41-8, 25167-67-3)	**SPONSORED CHEMICAL Butadiene Unit Heavy Ends Stream (69103-05-5, 68477-41-8, 68512-91-4)**	**SUPPORTING CHEMICAL 1,3-Butadiene (106-99-0)**
		NOAEC = 13.3 mg/L/day (highest concentration tested) (RA)	**NOAEC = 13.3 mg/L/day (highest concentration tested)**
Developmental Toxicity NOAEC/LOAEC Inhalation (ppm/day)			
Maternal Toxicity	**(rat) NOAEC = 20 mg/L/day[2] (highest concentration tested)**	No Data (rat) NOAEC = 20 mg/L/day[2] (RA)	**(rat) NOAEC = 3.3 mg/L/day[3] LOAEC = 0.66**
Developmental Toxicity (vapor)	**NOAEC = 20 mg/L/day[2] (highest concentration tested)**		**NOAEC = 13.3 mg/L/day[3] (highest concentration tested)**
Maternal/Developmental Toxicity (gas)	No data (rat) NOAEC = Not Established[3] LOAEC = 200 (RA) No data (mouse) NOAEC = 40[3] LOAEC = 200 (RA)	No data (rat) NOAEC = Not Established[3] LOAEC = 200 (RA) No data (mouse) NOAEC = 40[3] LOAEC = 200 (RA)	**(rat) NOAEC = Not Established[3] LOAEC = 200** **(mouse) NOAEC = 40[3] LOAEC = 200**
Genetic Toxicity – Gene Mutation *In vitro*	**Positive[1]**	No data Positive[1,3] (RA)	**Positive[3]**
Genetic Toxicity – Chromosomal Aberrations *In vivo*	**Positive[1,2,]**	No data Positive[1,2,3] (RA)	**Positive[3]**
Genetic Toxicity – Other *In vitro* Unscheduled DNA Synthesis	**Positive'[1]**	No data Positive[1] (RA)	–

Table 5. Summary of the Screening Information Data Setunder the U.S. HPV Challenge Program - Human Health Data

Endpoints	Crude Butadiene C4 Category		
	SPONSORED CHEMICAL C4 Crude Butadiene Stream (68476-52-8, 68187-60-0 68955-28-2, 64742-83-2 68476-44-8, 68956-54-7 68477-41-8, 25167-67-3)	SPONSORED CHEMICAL Butadiene Unit Heavy Ends Stream (69103-05-5, 68477-41-8, 68512-91-4)	SUPPORTING CHEMICAL 1,3-Butadiene (106-99-0)
Additional Information			
Skin Irritation	**Not irritating**[1]	–	–
Eye Irritation	**Not irritating**[1]	–	–
Carcinogenicity	–	–	**Positive**[3]

RA = Read Across; − indicates that endpoint was not addressed for this chemical; [1]Data from 68955-28-2 (45% or 67% 1,3-butadiene); [2]Data from CASRN 68476-52-8 (10% 1,3-butadiene); [3]Data from CASRN 106-99-0 (>99% 1,3-butadiene);

4. Hazard to the Environment

A summary of aquatic toxicity data submitted for SIDS endpoints is provided in Tables 6. The table also indicates where data for tested supporting chemicals are used to read-across (RA) for the untested members of the category.

Acute Toxicity to Fish

Pentane (CASRN 109-66-0, supporting chemical)
Rainbow trout (*Oncorhynchus mykiss)* were exposed to CASRN 109-66-0 for 96 hours. No other details were given: http://ecb.jrc.it/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/n-pentanereport043.pdf.
96-h LC_{50} = 4.26 mg/L

2-Butene, 2-methyl- (CASRN 513-35-9, supporting chemical)
Rainbow trout (*Oncorhynchus mykiss*) were exposed to CASRN 513-35-9 at nominal concentrations of 0, 2.13, 4.7, 10.3, 22.7 or 50 mg/L under static renewal conditions for 96 hours. Mean measured concentrations were 0, 1.67, 2.93, 5.33, 8.51 and 25.9 mg/L. Mortality was observed at concentrations ≥ 5.33 mg/L. One hundred percent mortality was observed at ≥ 8.51 mg/L (http://www.chem.unep.ch/irptc/sids/OECDSIDS/513359.pdf).
96-h LC_{50} = 4.99 mg/L

Ethylene (CASRN 74-85-1)
No acute toxicity data to fish is available for CASRN 74-85-1. ECOSAR (v. 1.00a) was used to estimate toxicity.
96-h LC_{50} = 95.7 mg/L

Acute Toxicity to Aquatic Invertebrates

Pentane (CASRN 109-66-0, supporting chemical)
Daphnia magna were exposed to CASRN 109-66-0 for 48 hours. No other details were given: http://ecb.jrc.it/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/n-pentanereport043.pdf.
48-h EC_{50} = 2.7 mg/L

2-Butene, 2-methyl- (CASRN 513-35-9, supporting chemical)
Daphnia magna were exposed to CASRN 513-35-9 at nominal concentrations of 2.13, 4.7, 10.3, 22.7 or 50 mg/L under static conditions for 48 hours. Mean measured concentrations were 0.691, 1.74, 2.95, 6.63 and 23.6 mg/L. (http://www.chem.unep.ch/irptc/sids/OECDSIDS/513359.pdf).
48-h EC_{50} = 3.84 mg/L

Ethylene (CASRN 74-85-1)
No acute toxicity data for aquatic invertebrates is available for CASRN 74-85-1. ECOSAR (v. 1.00a) was used to estimate toxicity.
48-h EC_{50} = 48.4 mg/L

Toxicity to Aquatic Plants

Pentane (CASRN 109-66-0, supporting chemical)
Green algae (*Pseudokirchneriella subcapitata*) were exposed to CASRN 109-66-0 for 72 hours. No other information was provided: http://ecb.jrc.it/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/n-pentanereport043.pdf.
72-h EC_{50} = 7.5 mg/L (biomass)
72-h EC_{50} = 10.7 mg/L (growth rate)

2-Butene, 2-methyl- (CASRN 513-35-9, supporting chemical)
Green algae (Pseudokirchneriella subcapitata) were exposed to CASRN 513-35-9 at nominal concentrations of 0, 3.20, 7.04, 15.5, 34.1 and 75.0 mg/L for 96 hours. Mean measured concentrations were 0, 0.689, 1.53, 3.61, 7.22 and 21.1 mg/L. (http://www.chem.unep.ch/irptc/sids/OECDSIDS/513359.pdf).
72-h EC_{50} = 10.5 mg/L (biomass)
72-h EC_{50} = 12.0 mg/L (growth rate)

Ethylene (CASRN 74-85-1, supporting chemical)
Green algae (*Pseudokirchneriella subcapitata*) were exposed to CASRN 74-85-1 at nominal concentrations of 8.2 – 131 mg/L for 72 hours. Mean measured concentrations were 3.3, 7.8, 13.9, 32 and 58 mg/L. Growth inhibition was observed at concentrations ≥ 32 mg/L. During the

72 hr exposure period there was a loss of ethylene in the range of 64-91 %, however in calculation of results the mean measured ethylene concentration was used (http://www.chem.unep.ch/irptc/sids/OECDSIDS/74851.pdf.)
72-h EC_{50} (biomass) = 40 mg/L
72-h EC_{50} (growth) = 72 mg/L

Conclusion: Based on the supporting chemicals, the 96-h LC_{50} for fish is 4.26 mg/L (CASRN 109-66-0), the 48-h EC_{50} for aquatic invertebrates is 2.7 mg/L (CASRN 109-66-0), and the 72-h EC_{50} for aquatic plants ranges from 7.5 (CASRN 109-66-0) to 40 mg/L (CASRN 74-85-1) for biomass and 10.7 (CASRN 109-66-0) to 72 mg/L (CASRN 74-85-1) for growth rate.

Table 6. Summary of the Screening Information Data Set as Submitted under the U.S. HPV Challenge Program – Aquatic Toxicity Data

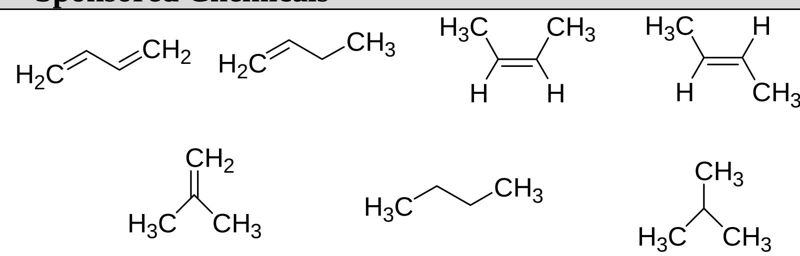
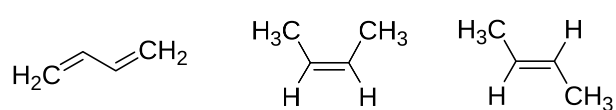
Endpoints	SUPPORTING CHEMICAL Ethylene (74-85-1)	SPONSORED CHEMICAL C4 Crude Butadiene (68476-52-8, 68187-60-0 68955-28-2, 64742-83-2 68476-44-8, 68956-54-7 68477-41-8, 25167-67-3)	SPONSORED CHEMICAL Butadiene Unit Heavy Ends (69103-05-5 68477-41-8 68512-91-4)	SUPPORTING CHEMICAL 2-Butene, 2-methyl- (513-35-9)	SUPPORTING CHEMICAL *n*-Pentane (109-66-0)
Fish 96-h LC_{50} (mg/L)	-	No Data 4.26 (RA)	No Data 4.26 (RA)	**4.99**	**4.26**
Aquatic Invertebrates 48-h EC_{50} (mg/L)	-	No Data 2.7 (RA)	No Data 2.7 (RA)	**3.84**	**2.7**
Aquatic Plants 72-h EC_{50} (mg/L) Biomass Growth rate	**40** **72**	No Data 7.5 – 40 10.7 – 72 (RA)	No Data 7.5 – 40 7.5 – 72 (RA)	**10.5** **12**	**7.5** **10.7**

bold = measured data (i.e., derived from testing); (e) = estimated data (i.e., derived from modeling); (RA) = Read-Across; − indicates that endpoint was not addressed for this chemical

APPENDIX

The following pages show:

- Table 7 shows representative structures of the sponsored substances and the supporting chemicals
- Table 8 provides names and TSCA definitions of the CAS numbers included in the category as provided by US EPA.
- Description of ethylene manufacturing process and the associated diagram are taken from the sponsor's original HPV submission of Crude Butadiene C4 Category—May 2000) ((http://www.epa.gov/oppt/chemrtk/pubs/summaries/olefins/c12064tc.htm)

Table 7		
Name	**CASRN**	**Description or Chemical Structure***
Sponsored Chemicals		
C4 Crude Butadiene Stream	106-99-0; 68476-52-8; 68187-60-0; 68955-28-2; 64742-83-2; 68476-44-8; 68956-54-7; 68477-41-8; 25167-67-3	 Representative structures This stream is produced from the distillation of a liquefied portion of cracked gas. This stream typically contains approximately 40 to 60% 1,3-butadiene. However, it can contain as little as 10% or as much as 82% 1,3-butadiene. Other hydrocarbons in this stream are predominately C4.
Butadiene Unit Heavy Ends Stream	106-99-0; 69103-05-5; 68477-41-8; 68512-91-4	 Representative structures This stream is produced from extractive distillation. This stream contains approximately 13 to 92% 1,3-butadiene. Other hydrocarbons in this stream are predominately C4.

An additional mixture, Residues (petroleum), deethanizer tower (CASRN 68513-68-8) was removed from this category and placed in Pyrolysis C3+ and Pyrolysis C4+ category

* Some of these compounds have TSCA definitions as part of the Chemical Identity See Table 8.

Table 8. TSCA Definitions as provided by US EPA.		
CASRN	**Chemical Name**	**TSCA Definition**
64742-83-2	Naphtha (petroleum), light steam-cracked	A complex combination of hydrocarbons obtained by the distillation of the products from a steam cracking process. It consists predominantly of unsaturated hydrocarbons having carbon numbers predominantly in the range of C4 through C11 and boiling in the range of approximately minus 20.degree.C to 190.degree.C (-4.degree.F to 374.degree.F). This steam is likely to contain 10 vol. % or more benzene.[1]
68187-60-0	Hydrocarbons, C4, ethane-propane-cracked	A complex combination of hydrocarbons obtained from the thermal cracking of a mixture of ethane and propane. It consists predominantly of C4 hydrocarbons.
68476-52-8	Hydrocarbons, C4, ethylene-manuf.-by-product	A complex combination of hydrocarbons produced by distillation of products from a cracking process in an ethylene plant. It consists predominantly of C4 hydrocarbons.
68477-41-8	Gases (petroleum), extractive, C3-5, butadiene-butene-rich	A complex combination of hydrocarbons obtained from oxydehydrogenation and extractive distillation of aliphatic hydrocarbons usually ranging in carbon numbers from C3 through C6, predominantly n-butylenes. It consists of aliphatic hydrocarbons having carbon numbers in the range of C3 through C5, predominantly butadiene and n-butylenes.
68512-91-4	Hydrocarbons, C3-4-rich, petroleum distillates	A complex combination of hydrocarbons produced by distillation and condensation of crude oil. It consists of hydrocarbons having carbon numbers in the range of C3 through C5, predominantly C3 through C4.
68955-28-2	Gases (petroleum), light steam-cracked, butadiene conc.	A complex combination of hydrocarbons produced by the distillation of products from a thermal cracking process. It consists of hydrocarbons having a carbon number predominantly of C4.
69103-05-5	Hydrocarbons, C4-7, butadiene manuf. by-product	A complex combination of hydrocarbons produced by distillation of products from butadiene production. It consists of hydrocarbons having carbon numbers predominantly in the range of C4 through C7. [2]

1. The presence of benzene [up to 10%] makes this chemical inappropriate for this category.
2. This by-products stream is likely to be predominantly C4 content..

ETHYLENE PROCESS DESCRIPTION

A. The Ethylene Process

1. <u>Steam Cracking</u>

Steam cracking is the predominant process used to produce ethylene. Various hydrocarbon feedstocks are used in the production of ethylene by steam cracking, including ethane, propane, butane, and liquid petroleum fractions such as condensate, naphtha, and gas oils. The feedstocks are normally saturated hydrocarbons but may contain minor amounts of unsaturated hydrocarbons. These feedstocks are charged to the coils of a cracking furnace. Heat is transferred through the metal walls of the coils to the feedstock from hot flue gas, which is generated by combustion of fuels in the furnace firebox. The outlet of the cracking coil is usually maintained at relatively low pressure in order to obtain good yields to the desired products. Steam is also added to the coil and serves as a diluent to improve yields and to control coke formation. This step of the ethylene process is commonly referred to as “steam cracking” or simply “cracking” and the furnaces are frequently referred to as “crackers”.

Subjecting the feedstocks to high temperatures in this manner results in the partial conversion of the feedstock to olefins. In the simplest example, feedstock ethane is partially converted to ethylene and hydrogen. Similarly, propane, butane, or the hydrocarbon compounds that are associated with the liquid feedstocks are also converted to ethylene. Other valuable hydrocarbon products are also formed, including other olefins, diolefins, aromatics, paraffins, and lesser amounts of acetylenes. These other hydrocarbon products include compounds with two or more carbon atoms per molecule, i.e., C2, C3, C4, etc. Propane and propylene are examples of C3 hydrocarbons and benzene, hexene, and cyclohexane are a few examples of the C6 hydrocarbons.

2. <u>Refinery Gas Separation</u>

Ethylene and propylene are also produced by separation of these olefins streams, such as from the light ends product of a catalytic cracking process. This separation is similar to that used in steam crackers, and in some cases both refinery gas streams and steam cracking furnace effluents are combined and processed in a single finishing section. These refinery gas streams differ from cracked gas in that the refinery streams have a much narrower carbon number distribution, predominantly C2 and/or C3. Thus the finishing of these refinery gas streams yields primary ethylene and ethane, and/or propylene and propane.

B. Products of the Ethylene Process

The intermediate stream that exits the cracking furnaces (i.e., the furnace effluent) is forwarded to the finishing section of the ethylene plant. The furnace effluent is commonly referred to as “cracked gas” and consists of a mixture of hydrogen, methane, and various hydrocarbon compounds with two or more carbon atoms per molecule (C2+). The relative amount of each component in the cracked gas varies depending on what feedstocks are cracked and cracking process variables. Cracked gas may also contain relatively small concentrations of organic sulfur compounds that were present as impurities in the feedstock or were added to the feedstock to control coke formation. The cracked gas stream is cooled, compressed and then separated into the individual streams of the ethylene process. These streams can be sold commercially and/or put into further steps of the process to produce additional materials. In some ethylene processes, a liquid fuel oil product is produced when the cracked gas is initially cooled. The ethylene process is a closed process and the products are contained in pressure systems. (See figure 1 for a pictorial representation of the ethylene manufacturing process.)

The final products of the ethylene process include hydrogen, methane (frequently used as fuel), and the high purity products ethylene and propylene. Other products of the ethylene process are typically mixed streams that are isolated by distillation according to boiling point ranges. It is a subset of these mixed streams that make up the constituents of the Crude Butadiene C4 category.

C. The Crude Butadiene C4 Products

1. Crude Butadiene Or Butadiene Concentrate

Butadiene concentrate is the product in the C4 Crude Butadiene Category. The concentrate is separated by distillation from the condensed portion of the cracked gas. Typically, butadiene concentrate is a fairly narrow boiling range mixture and consists predominately of C4 hydrocarbons. The butadiene concentrate may also contain lesser amounts of C3 or lighter hydrocarbons and C5 and heavier hydrocarbons, because the separation technology is not perfect. The 1,3-butadiene content of this product is typically 40% to 60%, but has been reported to range from 10% to about 80% (table 2). Crude butadiene is sometimes produced in "on purpose" butadiene units using, for example, an oxydehydrogenation process.

2. High Butadiene-Content Heavy Ends from The Butadiene Plant

Several different technologies are used to separate 1,3-butadiene from C4 butadiene concentrate produced by the ethylene process. All of these processes use a solvent for the separation.

In one technology, the C4 butadiene concentrate is fed to an extractive distillation (ED) column and a C4 mixture referred to as “raffinate” (i.e., C4 olefins and paraffins) is separated from the top of the distillate column. The bottom from the ED column consists of the solvent, rich in 1,3-butadiene, and small amounts of other C4s. The rich solvent is fed to the solvent stripper where the 1,3-butadiene and other C4s are taken overhead. The stripped, lean solvent is transferred from the bottom of the stripper back to the ED tower.

Stripper is condensed and fed to the rerun tower (or postfractionator) where high purity 1,3butadiene is produced as the overhead. Bottoms of the rerun tower consist of the higher boiling components of the butadiene concentrate (e.g., 1,2-butadiene). The 1,3-butadiene content of the heavy ends from the butadiene plant covered by this test plan ranges from 13% to 92% (Table 2).

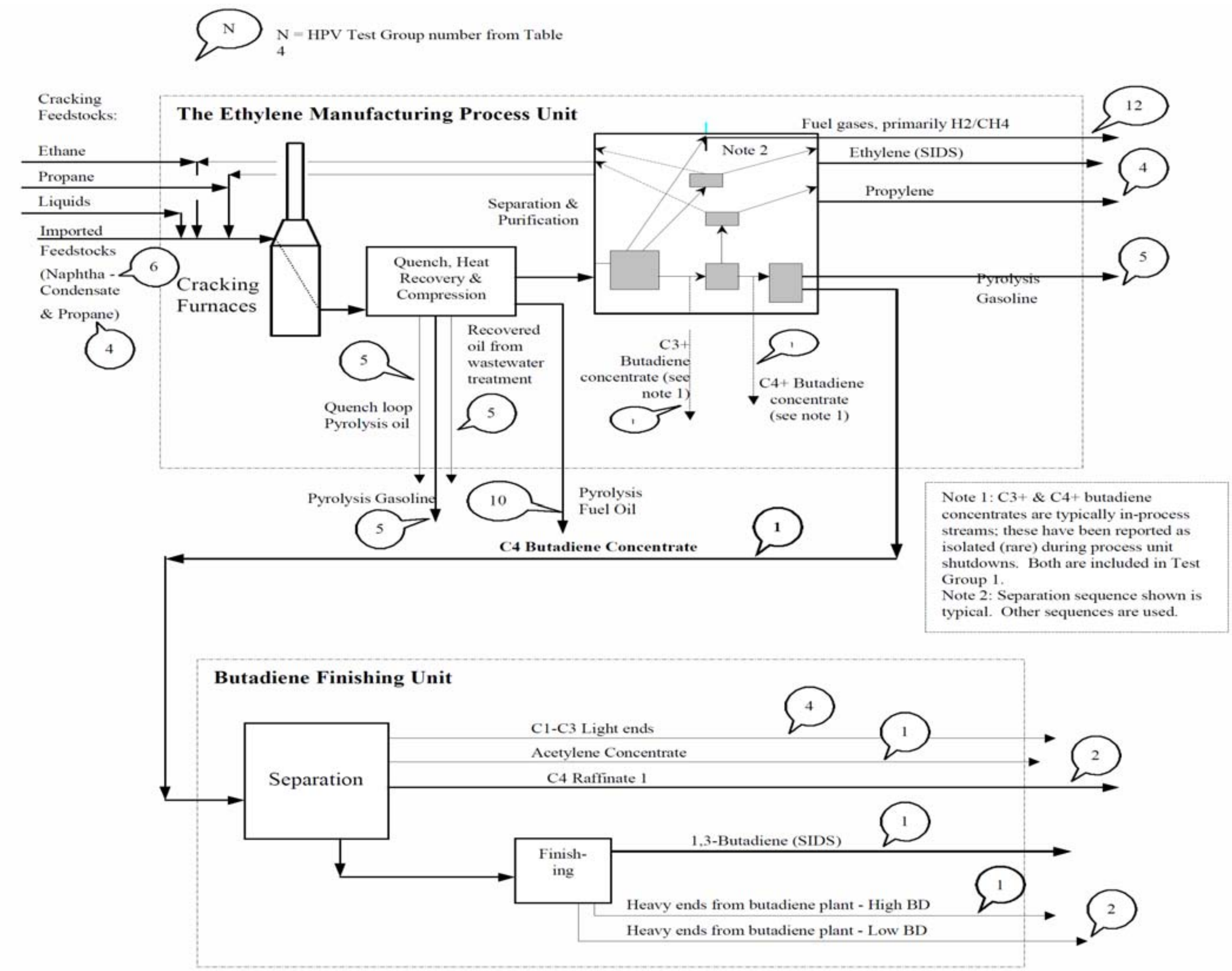
3. Full-Range Butadiene Concentrate

Butadiene concentrate sometimes consists of the entire C3+ or C4+ portion of the cracked gas stream (full-range butadiene concentrate). In this case, the carbon number distribution is between C3 and C12 or even higher. Normally the C4+ full-range butadiene concentrate is split by distillation into two streams, a butadiene concentrate stream, described above, and pyrolysis gasoline stream. The C3+ stream is separated into these two streams plus a C3 stream. The C3 stream and pyrolysis gasoline will be covered by separate test categories sponsored by the CMA Olefins Panel. There are only two known examples where these broad-range streams have been reported to have been isolated. In both cases, it was a result of a shutdown of process equipment. The C4+ stream was site limited and the C3+ was not. The 1,3-butadiene content of full range butadiene concentrate has been reported to range from 12% to 42% (Table 2).

4. 1,3-Butadiene

High purity 1,3-butadiene (99.5%+) is produced by separation from the C4 butadiene concentrate (or crude butadiene) produced by the ethylene process. This separation is accomplished by using a solvent process, either extraction or more typically extractive distillation. "On purpose" units also produce a small percentage of the commercially available 1,3 butadiene by dehydrogenation and subsequent separation.

Ethylene Process Streams (sponsored under the HPV Challenge Program) as presented in the Test Plan (May 1, 2000)



1. Crude Butadiene C4
2. Low Butadiene C4
3. C5 Non-Cyclics
4. Propylene Streams (C3)
5. High Benzene Naphthas (C6-C12, predominantly C6)
6. Low Benzene Naphthas (C7-C12)
7. Resin Oil - High Dicyclopentadiene
8. Resin Oil - Low Dicyclopentadiene
9. Resin Oil - Dicyclopentadiene Concentrate and Crude Dicyclopentadiene
10. Fuel Oils (C8+)
11. Fuel Gases