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## **US High Production Volume Chemical Program**

### **Category Summary**

**For**

### **Low 1,3-Butadiene C4 Category**

**Prepared by:**

**Olefins Panel of the American Chemistry Council**

**August 20, 2004**

## EXECUTIVE SUMMARY

The Olefins Panel of the American Chemistry Council (ACC) hereby submits the category summary report for the Low 1,3-Butadiene C4 Category under the Environmental Protection Agency's High Production Volume (HPV) Chemical Challenge Program (Program). The purpose of this report is to:

- Present results of an assessment to determine whether seven production streams can be adequately characterized with existing data and additional data as described in the Low 1,3-Butadiene C4 Category test plan.
- Summarize the SIDS (Screening Information Data Set) physicochemical, environmental fate and effects, and human health HPV Program endpoints for the Low 1,3-Butadiene C4 Category.
- Provide a description of manufacturing processes, potential exposure sources, and uses for Low 1,3-Butadiene C4 streams.

The Low 1,3-Butadiene C4 Category contains seven streams. After all data were evaluated to determine whether the streams formed a cohesive category, it was decided that they could be considered a category. The following category report summarizes HPV Program data for the Low 1,3-Butadiene C4 Category.

The seven streams in the Low 1,3-Butadiene C4 Category include four process streams that are complex mixtures while the remaining three describe high purity hydrocarbons. The CAS numbers used to represent the four mixed streams are generally vague with respect to the specifics that distinguish the streams within the category. Therefore, more than one CAS number may correctly represent a single stream and a CAS number may be applicable to more than one stream. A process stream is a mixture of chemicals that arises from a chemical reaction or separation activity.

### Exposure

Discussion of the use of and potential exposure to Low 1,3-Butadiene C4 category members is limited to 1-butene and the four mixed C4 streams. The category mixed streams contain low levels (typically <1%) of 1,3-butadiene. The major stream in the category is C4 Raffinate 1 (69% of the production volume) and the other category streams are isolated from this stream, with the exception of catalytic butylenes (a refinery process stream). A discussion of potential for exposure to the production and use of motor gasoline streams within the petroleum refinery industry was not included in this assessment.

Category streams are either used (further processed) on site or transported in bulk to other industrial sites for processing. When transported, the category streams are moved in bulk quantities by pipeline, pressure barge, ship, tank car, and tank truck. Butene-1 is also shipped in smaller bulk containers.

All of the 11 billion pound production of selected category streams per year is consumed as chemical intermediates in other chemical manufacturing or refinery processes. There are no consumer uses of category streams. The major uses of category streams include production of the motor gasoline additive MTBE (53%), feedstock for motor gasoline production (28%), and intermediates for plastic and other chemical production (19%).

The category streams are gases at ambient conditions and inhalation is the most likely route of exposure. Category streams are produced, stored and transported in closed, pressurized systems, and therefore there is no direct worker contact with the streams. Potential for exposure of workers at the olefins process units where category streams are produced and used occurs from fugitive emission sources (equipment leaks) and from other potential emissions from the closed process.

Emissions from these sources also present a potential for exposure to the environment and to areas bordering production facilities.

The general public may also be exposed to butene-1 from sources other than from category streams. Butene-1 is reported to be a naturally occurring emission from trees and found in soybean, rapeseed, peanut, and Canola oil. Some of the individual components that make up the Category streams also are present in the environment. Butene-2 and isobutane, for example, are found in engine exhaust and fuels. Isobutane is used as a propellant, for example in insect sprays, deodorants, and rug and upholstery cleaners.

Neither OSHA (Occupational Safety and Health Administration) nor ACGIH<sup>1</sup> have established exposure limits for the streams in the Category or for any of the components that are present in significant concentrations, with the exception of 1,3-butadiene. Category streams (except butene-1, C4 raffinate 3, and butane) contain low levels of 1,3-butadiene, typically in the range of 0.1 to 5.0%. Unless exempted, facilities that use or produce these Category streams are subject to the OSHA Butadiene standard (29 CFR 1910.1051) which limits occupational exposures to 1,3-butadiene to 8-hr time-weighted-average limit of 1 ppm and a short-term (15 minutes) limit of 5 ppm.

ACGIH adopted a TLV for butane of 800 ppm, based on the effect of narcosis. Butane, which accounts for approximately 88% of the butane stream, is typically present at concentrations between 1% and 55% in the mixed category streams (C4 Raffinate 1, C4 Raffinate 2, and C4 Raffinate 3, and Catalytic Butylenes). EPA and individual states enforce a number environmental requirements intended to limit emissions of volatile organic compounds (VOC), which includes all of the category streams.

Expected ground level concentrations for butene-1 in U.S. urban air range from 1 to 20 ppb. Average annual mean value at selected industrial sites in Texas was 1.07 ppb (1994 through 1997). At the same Texas sites and time period, the average annual mean values for trans-butene-2, cis-butene-2, and isobutane (hydrocarbon components included in the complex category streams) were 0.37, 0.21, and 4.20 ppb.

A NIOSH report estimates 545 workers were potentially exposed to butene-1 (1981-1983).

### **Human Health**

Low 1,3-Butadiene C4 streams have a low order of acute toxicity. No lethality was observed at the limit concentration for 2-butene, and, other than restlessness, no toxicity was observed either. The 15-minute LC<sub>50</sub> for isobutane was >570,000 ppm and the 4-hour LC<sub>50</sub> for n-butane was 276,000 ppm. Similar results would be anticipated with other components of streams in the Low 1,3-Butadiene C4 Category. 2-Butene enantiomers were the most potent C4 olefin to induce cardiac arrest in mice after exposure to remarkably high concentrations for 20 minutes. Isobutylene and 1-butene were less potent. Thus it is reasonable to extrapolate the findings of the guideline acute toxicity study of 2-butene across the other components of the Low 1,3-Butadiene C4 Category.

There are no dermal or ocular irritation data on Low 1,3-Butadiene C4 streams or components. Read-across from studies of the Crude butadiene C4 Category was used. No dermal or ocular irritation was observed in these studies, likely due to the rapid evaporation of the test substance. As the streams in the Low 1,3-Butadiene C4 Category are gases at normal temperature and pressure, similar results would be expected.

Minimal effects were reported in repeat dose toxicity tests of several components of Low 1,3-Butadiene C4 streams. Reduced body weights were observed in male and female rats exposed to 2-

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<sup>1</sup> Formerly known as the American Conference of Governmental Industrial Hygienists, now referred to only by the acronym.

butene resulting in a NOAEL of 2500 ppm. A reduction in white blood cell count was observed in rats following oral exposure to 148.55 mg/kg/day isobutylene for 28 days. No adverse treatment related effects were observed in rats exposed to isobutylene for 90 days or 1-butene for 28 days via inhalation.

Test data demonstrate that Low 1,3-Butadiene C4 streams do not produce genotoxicity. No mutagenic activity was observed in *Salmonella typhimurium* reverse mutation assays in the presence or absence of metabolic activation following treatment with isobutylene, 1-butene, 2-butene, isobutane, or n-butane. In addition, isobutylene did not increase the number of transformed foci in mouse embryo fibroblast cells. In the mouse lymphoma assay, no evidence of mutagenic activity in mouse lymphoma L5178Y cells treated with isobutylene in culture in the presence or absence of metabolic activation. No chromosomal aberrations were observed following *in vitro* treatment with 2-butene (with and with out activation), or *in vivo* treatment with isobutylene or 1-butene. As such the Low 1,3-Butadiene C4 Category presents a low genotoxicity hazard.

Available data indicate little reproductive or developmental hazard with the streams in Low 1,3-Butadiene C4 Category. No reproductive or developmental toxicity was observed in rats exposed to either 1-butene or 2-butene during the conduct of an OECD (Organization for Economic Cooperation and Development) 422 combined repeat dose reproductive and developmental toxicity screen. No maternal or developmental effects were observed following exposure to isobutylene during gestation. No effect on reproductive organs was observed following repeated exposure to isobutylene in a well-conducted ninety-day subchronic toxicity study. Additionally, no reproductive or developmental effects were observed in rats exposed to C4 olefin containing streams in the Crude Butadiene C4 Category. Results from reproductive developmental toxicity studies on isobutane and n-butane were not available at the time this report was written. However, study results on these two materials will become available as part of the API Petroleum HPV Testing Group Petroleum Gases Test Plan.

### **Environment**

Results of distribution modeling show that chemical constituents of streams in the Low 1,3-Butadiene C4 Category will partition primarily to the air compartment, with a negligible amount partitioning to water. In the air, these constituents have the potential to rapidly degrade through indirect photolytic processes mediated primarily by hydroxyl radicals. This is expected to be the dominant route of loss and degradation process for constituents of these streams. Aqueous photolysis and hydrolysis will not contribute to the transformation of category constituents in aquatic environments because they are either poorly or not susceptible to these reactions.

Although the biodegradability of streams in this category has not been evaluated with standard testing procedures because of their high volatility, studies have demonstrated that several category constituents can be degraded by bacteria isolated from soil and surface water samples. The results from these studies show that selected stream constituents are subject to microbial degradation. However, biodegradation is unlikely to contribute to the overall degradation of constituents from these streams because they tend to partition to the air compartment.

Due to the fact that streams in this category are gaseous at ambient temperature and pressure and expected to partition predominantly to the atmosphere, aquatic toxicity testing was not conducted. However, aquatic toxicity was assessed with a model that is based on an equation developed for neutral organic chemicals, a reliable estimation method for the class of chemicals in streams from this category. Calculated toxicity values for two to four day exposures suggest that category members have the potential to produce moderate toxicity, based on an effect range of 4.71 to 43.88 mg/L for selected stream constituents.

**OLEFINS PANEL of the AMERICAN CHEMISTRY COUNCIL  
MEMBER COMPANIES**

ATOFINA Petrochemicals, Inc.\*  
BP Amoco, p.l.c.  
Chevron Phillips Chemical Company LP  
The Dow Chemical Company\*  
E. I. du Pont de Nemours and Company\*  
Eastman Chemical Company\*  
Equistar Chemicals, LP  
ExxonMobil Chemical Company  
Flint Hills Resources\*  
Formosa Plastics Corporation, U.S.A.\*  
The Goodyear Tire & Rubber Company\*  
Huntsman Corporation  
NOVA Chemicals Inc.\*  
Noveon, Inc.\*  
Sasol North America, Inc.\*  
Shell Chemical LP  
Sunoco, Inc.\*  
Texas Petrochemicals LP  
Westlake Chemical Corporation\*  
Williams Olefins, LLC\*

\* Companies that are part of the Olefins Panel, but do not produce substances covered by the Low 1,3-Butadiene C4 Category.

## TABLE OF CONTENTS

<a href="#">EXECUTIVE SUMMARY</a> .....	ii
<a href="#">OLEFINS PANEL OF THE AMERICAN CHEMISTRY COUNCIL MEMBER COMPANIES</a> .....	v
1 CATEGORY DESCRIPTION AND JUSTIFICATION .....	1
1.1 Category Identification .....	1
1.2 Purity/Impurities/Additives .....	4
1.3 Physico-Chemical Properties .....	4
1.3.1 Melting Point (Range) .....	5
1.3.2 Boiling Point (Range) .....	5
1.3.3 Vapor Pressure (Range) .....	5
1.3.4 Log P <sub>ow</sub> (Range) .....	5
1.3.5 Water Solubility (Range) .....	6
1.4 Category Justification .....	6
2 EXPOSURE AND USE .....	6
3 ENVIRONMENTAL FATE .....	12
3.1 Photodegradation .....	12
3.1.1 Direct Photodegradation .....	12
3.1.2 Indirect Photodegradation .....	13
3.2 Stability in Water (Hydrolysis) .....	14
3.3 Distribution in the Environment .....	14
3.4 Biodegradation .....	15
3.4.1 Propylene Biodegradation .....	16
3.4.2 1,3-Butadiene Biodegradation .....	16
3.4.3 1-Butene Biodegradation .....	17
3.4.4 2-Butene Biodegradation .....	17
3.4.5 Isobutylene Biodegradation .....	17
3.4.6 Abiotic and Biotic Degradation Summary .....	17
4 HUMAN HEALTH HAZARDS .....	17
4.1 Effects on Human Health .....	18
4.1.1 Acute Toxicity .....	18
4.1.2 Irritation .....	19
4.1.3 Repeated Dose Toxicity .....	19
4.1.4 Mutagenicity .....	22
4.1.5 Toxicity for Reproduction .....	24
4.2 Assessment Summary for Human Health .....	27
5 HAZARDS TO THE ENVIRONMENT .....	28
5.1 Aquatic Toxicity .....	28
5.2 Assessment Summary for the Environment .....	29
6 DATA SUMMARY .....	30
7 REFERENCES .....	33

## Appendices

### APPENDIX I

<a href="#">ETHYLENE PROCESS DESCRIPTION</a> .....	36
A. <a href="#">Ethylene Process</a> .....	36
B. <a href="#">Products of the Ethylene Process</a> .....	36

### APPENDIX II

ROBUST SUMMARIES OF STUDIES USED TO CHARACTERIZE THE LOW 1,3-BUTADIENE C4 CATEGORY .....	39
PHYSICO-CHEMICAL ROBUST SUMMARIES.....	39
ENVIRONMENTAL FATE ROBUST SUMMARIES .....	56
HUMAN HEALTH ROBUST SUMMARIES.....	84
AQUATIC TOXICITY ROBUST SUMMARIES .....	136

## Tables

<a href="#">Table 1. Production Streams, CAS RNs, and CAS RN Names in the Low 1,3- Butadiene C4 Category</a> .....	1
<a href="#">Table 2. Typical Constituent (wt%) Range in Streams of the Low 1,3-Butadiene C4 Category</a> .....	2
<a href="#">Table 3. Summary of Calculated Physico-Chemical Properties for Selected Chemicals Contained by Streams in the Low 1,3-Butadiene C4 Category</a> .....	4
<a href="#">Table 4. Summary of Measured Physico-Chemical Properties for Selected Chemicals Contained by Streams in the Low 1,3-Butadiene C4 Category</a> .....	5
<a href="#">Table 5. Ambient Air Monitoring Data at Various Texas Industrial Sites (1994 through 1997)</a> .....	10
<a href="#">Table 6. Characteristic Absorbance Maxima (<math>\lambda_{max}</math>) and Associated Molar Absorptivities (<math>\epsilon</math>) for Two Unsaturated Hydrocarbons from Streams in the Low 1,3-Butadiene C4 Category</a> .....	13
<a href="#">Table 7. Hydroxyl Radical Photodegradation Half-life of Selected Chemicals from Streams in the Low 1,3-Butadiene C4 Category</a> .....	13
<a href="#">Table 8. Environmental Distribution as Calculated by the EQC Level I Fugacity Model for Selected Chemicals from Streams in the Low 1,3-Butadiene C4 Category</a> .....	15
<a href="#">Table 9. Summary of Acute Inhalation Toxicity Data for the Low 1,3-Butadiene C4 Category</a> .....	18
<a href="#">Table 10. Summary of Repeated Dose Toxicity Data for the Low 1,3-Butadiene C4 Category</a> .....	20
<a href="#">Table 11. Summary of Reproductive Toxicity Data for the Low 1,3-Butadiene C4 Category</a> .....	24
<a href="#">Table 12. Summary of Developmental Toxicity Data for the Low 1,3-Butadiene C4 Category</a> .....	25
<a href="#">Table 13. Summary of Aquatic Toxicity Data for Chemical Constituents in the Low 1,3-Butadiene C4 Category</a> .....	29
<a href="#">Table 14. Physico-Chemical and Environmental Data Used to Characterize Streams and CAS Numbers in the Low 1,3-Butadiene C4 Category</a> .....	31
<a href="#">Table 15. Human Health Data Summary Used to Characterize Streams and CAS Numbers in the Low 1,3-Butadiene C4 Category</a> .....	32
<a href="#">Table 16. HPV Program Categories Sponsored by the Olefins Panel of the American Chemistry Council</a> .....	37

## Figures

<a href="#">Figure 1. Low 1,3-Butadiene C4 Category Production by Stream</a> .....	8
<a href="#">Figure 2. Uses of Low 1,3-Butadiene C4 Streams</a> .....	8
<a href="#">Figure 3. Proposed Microbial Metabolic Pathway for the Degradation of 1,3-Butadiene by a <i>Nocardia sp.</i></a> .....	16
<a href="#">Figure 4. Low 1,3-Butadiene C4 Process Streams Flow Diagram from the Ethylene Manufacturing Process Unit</a> ....	38

## 1 CATEGORY DESCRIPTION AND JUSTIFICATION

### 1.1 Category Identification

For purposes of the US High Production Volume (HPV) Chemical Challenge Program (Program), the Low 1,3-Butadiene C4 Category test plan submitted in July 2001 (Olefins Panel, HPV Implementation Task Group, 2001) included seven production streams and eight Chemical Abstracts Service (CAS) registration numbers (RNs). One CAS RN, 68606-24-6, has been added to the C4 Raffinate 3 stream, bringing to a total, nine CAS RNs covered under this category (Table 1). The test plan identified existing data and additional sources of data as well as data needed, based on an extensive technical review of the category, to adequately characterize the seven streams for the HPV Program endpoints.

**Table 1. Production Streams, CAS RNs, and CAS RN Names in the Low 1,3-Butadiene C4 Category<sup>1</sup>**

Production Streams	CAS RN	CAS RN Name
C4 Raffinate 1	68477-42-9	Gases, petroleum, extractive, C3-5, butene-isobutylene-rich
	25167-67-3	Butene
	68477-83-8	Gases, petroleum, C3-5 olefinic-paraffinic alkylation feed
	68527-19-5	Hydrocarbons, C1-4, debutanizer fraction
	68606-31-5	Hydrocarbons, C3-5, butadiene purifn by-product
C4 Raffinate 2	68606-31-5	Hydrocarbons, C3-5, butadiene purifn by-product
	25167-67-3	Butene
C4 Raffinate 3	68606-24-6 <sup>2</sup>	Hydrocarbons, C4, butene concentrator by-product
	25167-67-3	Butene
Catalytic Butylenes	25167-67-3	Butene
Butane	106-97-8	Butane
Butene-1	106-98-9	1-Butene
Isobutylene	115-11-7 <sup>3</sup>	1-Propene, 2- methyl

- 1 The definitions found in the TSCA Chemical Substance Inventory for the CAS RNs in this category are vague with respect to composition. Therefore, it is not uncommon to find that one CAS RN is correctly used to describe different streams (different compositions) or that two or more CAS RNs are used to describe one stream (similar composition). CAS RNs associated with corresponding production streams are shown in the above table. The Olefins Industry or others may use these same CAS RNs to represent substances that may, in various degrees, be dissimilar to the category streams.
- 2 This CAS RN was not included in the list of CAS RNs originally sponsored under this category. It has been added to this summary report because it is an additional CAS RN that is sometimes used to represent the C4 Raffinate 3 stream.
- 3 Although this CAS RN was listed in the Low 1,3-Butadiene C4 Category test plan submitted by the Olefins Panel, HPV Implementation Task Group, it was not sponsored under this category because adequate data were summarized for this substance under the OECD (Organization for Economic Co-operation and Development) SIDS (Screening Information Data Set) HPV (High Production Volume) Program. Data for this substance is being used to support the characterization of selected category endpoints.

The following category report summarizes HPV Program data for the Low 1,3-Butadiene C4 Category. The seven streams in the Low 1,3-Butadiene C4 Category include four process streams

that are complex mixtures (C4 Raffinate 1, C4 Raffinate 2, C4 Raffinate 3, and Catalytic Butylenes) while the remaining three (Butane, Butene-1, and Isobutylene) describe high purity hydrocarbons.

The streams in this category include complex hydrocarbon reaction products and relatively pure hydrocarbons with a carbon number distribution that is predominantly C4. The 1,3-butadiene content is generally less than one percent but on occasion may reach as high as five percent. With the exception of CAS RN 106-97-8 (butane) these streams contain significant levels of olefins. The typical compositions of the streams in this category are shown in Table 2.

**Table 2. Typical Constituent (wt%) Range in Streams of the Low 1,3-Butadiene C4 Category**

Constituent	C4 Raffinate 1 (wt%)	C4 Raffinate 2 (wt%)	C4 Raffinate 3 (wt%)	Catalytic Butylenes (wt%)	Butane (wt%)	Butene-1 (wt%)	Iso-butylene (wt%)
Acetonitrile	0-50*						
Carbonyl	0-50*						
Propylene		0 - 1					
Propane	1 - 5			1.2 - 1.3			
Propadiene	0 - 1	0 - 1					
Isobutane	0 - 65	1 - 7.5			3.5		
Isobutylene (Isobutene)	30 - 55	1 - 5		5			99.4
C5 Olefins							1.1
Butene-1	7 - 50	2.5 - 65	0.2			99.2	
1,3-Butadiene	0 - 5	0.1 - 0.5		0.5		0.005	0.1
Other C4s						1.4	
Butanes				40 - 46			
Butane	1 - 26	10 - 39	55.2		88.2		
Butenes				48 - 58			
Butene-2 (isomer mix)	1 - 50	11 - 55	45.2				
Isopentane (2-methyl-butane)					5.3		

\* ppm

Note 1: The balance of these streams is expected to include 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.

Existing toxicology data suggests that the most biologically active C4 hydrocarbon is 1,3-butadiene and that positive genotoxicity is the most sensitive health effect endpoint. The Low 1,3-Butadiene C4 Category consists of C4 process streams that have had most of the 1,3-butadiene content

removed or in the case of two streams, do not contain 1,3-butadiene. The 1,3-butadiene concentration is typically less than one percent but may range from zero to five percent in one stream. 1,3-Butadiene must be biotransformed prior to causing toxicity and other C4 alkenes are biotransformed through a common metabolic pathway. It is anticipated that mixed components will compete for the same active enzyme sites and that competition for the same active enzyme sites could lead to decreased production of toxic metabolites. Therefore, it is likely that the positive genotoxicity of 1,3-butadiene will be reduced or eliminated by the greater presence (greater than or equal to 95%) of the other components in those streams that contain 1,3-butadiene.

The TSCA Chemical Substance Inventory definitions for the CAS RNs in this and in other categories from the Olefins Panel's HPV Program can be vague with respect to composition. Therefore, it is not uncommon that a CAS RN is correctly used to describe different streams (different compositions) or that two or more CAS RNs are used to describe one stream (similar composition or process). For this reason, the data matrix for this category was developed based on seven compositionally differentiated process streams, rather than on the CAS RNs in this category.

The Low 1,3-Butadiene C4 streams arise from production processes associated with ethylene manufacturing (see Appendix I for a description of the ethylene and associated processes). Briefly, descriptions of the seven process streams are:

1. C4 Raffinate 1 (Raff 1) stream is a co-product of the butadiene extraction process unit. Raff 1 is the balance of the C4 butadiene concentrate after separation of butadiene by a solvent process, either extraction, or more typically extractive distillation. Raff 1 consists predominantly of C4 mono-olefins and C4 paraffins. This stream is sometimes referred to as mixed butylenes because the composition is often about 75% C4 mono-olefins. The saturated hydrocarbons in Raff 1 are mostly iso- and normal-butane. The mono-olefin content varies depending on the feedstock of the ethylene process unit that produced the C4 butadiene concentrate. For example, an ethylene unit that uses butane as cracking feedstock would yield a Raff 1 stream with much lower butanes content than an ethylene plant cracking ethane or propane feedstocks.
2. C4 Raffinate 2 (Raff 2) stream is produced from the C4 Raffinate 1 stream by additional processing to remove isobutylene. This is accomplished in a two-step process by reaction with water to make tertiary-butyl alcohol or with methanol to produce methyl-tertiary-butyl-ether, which can then be re-cracked to high purity isobutylene. Raff 2 consists predominantly of butene-1, butene-2, and butanes.
3. C4 Raffinate 3 (Raff 3) stream is produced from the C4 Raffinate 2 stream by additional processing to remove butene-1. It contains mixed butenes, including the cis- and trans-butene-2 isomers and sometimes n-butane.
4. Catalytic Butylenes stream refers to the C4 cut from a catalytic cracker (a petroleum refinery process). A typical composition is about 55% butenes and 45% butanes with a complete carbon number distribution of C3 to C5. The stream is relatively low in 1,3-butadiene and diolefins (a few tenths of a percent). In some cases the stream is a combination of catalytic cracker C4 butylenes and ethylene process C4 Raffinate 1 from the butadiene production unit.
5. Butane stream can be used as a feedstock for the ethylene process (Appendix I). An ethylene producer who operates an isobutylene alkylation process (typically a petroleum refinery process used to produce alkylates for gasoline formulations) lists butane from this source as a coproduct. Butane is also sometimes separated by distillation from C4 Raffinate 3.
6. Butene-1 (high purity) stream is produced by distillation from isobutylene plant raffinate.
7. Isobutylene stream, as discussed above, can be obtained from C4 Raffinate 1 by reaction with water or methanol and then re-cracking the product to high purity isobutylene. Alternately, isobutylene is obtained by isomerization of C4 Raffinate 2 or by dehydrogenation of isobutane.

Commercial isobutylene is typically 95% pure.

## 1.2 Purity/Impurities/Additives

Additives are not added to Low 1,3-Butadiene C4 streams prior to shipment.

## 1.3 Physico-Chemical Properties

The seven streams in this category include four that are complex, containing many different hydrocarbons (Table 2), that can vary in composition not only between manufacturers but also for an individual manufacturer, depending on feedstock type and operating conditions. The eight constituents listed in Tables 3 and 4 comprise significant proportions of these complex streams, which is why they were selected to represent the potential range of physico-chemical (PC) properties of these streams. The three relatively pure streams, butane, butene-1, and isobutylene are represented by the properties listed for those individual chemicals. Therefore, these data can be used to adequately characterize the five PC endpoints of substances in this category for the HPV Program.

**Table 3. Summary of Calculated Physico-Chemical Properties for Selected Chemicals Contained by Streams in the Low 1,3-Butadiene C4 Category**

Chemical	Melting Point (°C)	Boiling Point (°C)	Vapor Pressure (hPa@ 25°C)	Log P <sub>ow</sub>	Water Solubility (mg/L)
Isobutane	-132.6	3.2	3.45 E3	2.23	496.4
n-Butane	-120.3	19.6	2.41 E3	2.31	424.1
Isobutylene	-130.9	10.2	2.97 E3	2.23	495.6
cis-Butene-2	-120.4	27.8	2.31 E3	2.09	652.7
trans-Butene-2	-120.4	27.8	2.31 E3	2.09	652.7
Butene-1	-121.7	17.6	2.48 E3	2.17	557.7
1,2-Butadiene	-117.9	19.7	1.65 E3	2.06	687.8
1,3-Butadiene	-123.2	15.6	2.73 E3	2.03	732.4

Calculated values derived by the EPIWIN program (EPIWIN, 1999).

**Table 4. Summary of Measured Physico-Chemical Properties for Selected Chemicals Contained by Streams in the Low 1,3-Butadiene C4 Category**

Chemical	Melting Point (°C)	Boiling Point (°C)	Vapor Pressure (hPa@ 25°C)	Log P <sub>ow</sub>	Water Solubility (mg/L)
Isobutane	-138.3	-11.7	3.08 E3	2.76	175.1
n-Butane	-138.2	-0.5	2.43 E3	2.89	135.6
Isobutylene	-140.4	-6.9	3.08 E3	2.34	399.2
cis-Butene-2	-105.5	0.8	2.33 E3	2.31	423.5
trans-Butene-2	-105.5	0.8	2.33 E3	2.33	407.1
Butene-1	-145.0	-1.3	3.00 E3	2.40	354.8
1,2-Butadiene	-136.2	10.9	1.68 E3	na	na
1,3-Butadiene	-108.9	-4.4	2.81 E3	1.99	792.3

na not available

Measured values from the EPIWIN experimental database (EPIWIN, 1999).

The following sections identify the values used to define the five PC endpoints of the seven streams in this category.

### 1.3.1 Melting Point (Range)

Based on calculated values, the complex streams in this category can have a melting point range of -132.6 to -117.9°C. Based on measured values, the complex streams in this category can have a melting point range of -145.0 to -105.5°C. The calculated data compare favorably with the measured data. The measured data are considered the appropriate primary data set to characterize the melting point range of the complex streams.

### 1.3.2 Boiling Point (Range)

Based on calculated values, the complex streams in this category can have a boiling point range of 3.2 to 27.8°C. Based on measured values, the complex streams in this category can have a boiling point range of -11.7 to 10.9°C. The calculated data are not comparable with the measured data. The measured data are consistent with process knowledge and are considered the appropriate primary data set to characterize the boiling point range of the complex streams.

### 1.3.3 Vapor Pressure (Range)

Based on calculated values, the complex streams in this category can have a vapor pressure range of 1.65 E3 to 3.45 E3 hPa at 25°C. Based on measured values, the complex streams in this category can have a vapor pressure range of 1.68 E3 to 3.08 E3 hPa at 25°C. The calculated data compare favorably with the measured data. The measured data are consistent with process knowledge and are considered the appropriate primary data set to characterize the vapor pressure range of the complex streams.

### 1.3.4 Log P<sub>ow</sub> (Range)

Based on calculated values, the complex streams in this category can have a log P<sub>ow</sub> range of 2.03 to 2.31. Based on measured values, the complex streams in this category can have a log P<sub>ow</sub> range of 1.99 to 2.89. The calculated data compare favorably with the measured data for the unsaturated molecules, 2.03 to 2.23 vs. 1.99 to 2.40, respectively. In comparison, the calculated data for the

saturated molecules are not comparable with the measured data. The measured data are considered the appropriate primary data set to characterize the log  $P_{ow}$  range of the complex streams.

### 1.3.5 Water Solubility (Range)

Based on calculated values, the complex streams in this category can have a water solubility range of 424.1 to 732.4 mg/L. Based on measured values, the complex streams in this category can have a water solubility range of 135.6 to 792.3 mg/L. As with the log  $P_{ow}$  data, the calculated data compare favorably with the measured data for the unsaturated molecules, 495.6 to 732.4 mg/L vs. 354.8 to 792.3 mg/L, respectively. In comparison, the calculated data for the saturated molecules are not comparable with the measured data. The measured data are considered the appropriate primary data set to characterize the water solubility range of the complex streams.

## 1.4 Category Justification

After all data were evaluated to determine whether the streams formed a cohesive category, it was decided that they could be considered a category. Sufficient data were either identified or developed for the HPV Program to adequately characterize the human health and environmental endpoints for all members of this category.

The data used to characterize the human health endpoints of the streams in this category include data on the major C4 components including butene-1, butene-2, isobutylene, isobutane, and butane. At the time of this document's preparation, butene-1 and butene-2 were sponsored in the OECD SIDS program and as such, data will become available for these substances through this program. Isobutylene was sponsored in the OECD SIDS program in 2004. Isobutane and butane were evaluated as part of an American Petroleum Institute HPV test plan for the HPV program and as such, data will become available for these substances through this program.

Additionally, data from a repeat-dose reproductive/developmental screen for a C4 stream containing approximately 10% 1,3-butadiene, among other smaller molecular weight hydrocarbons, was used to characterize these endpoints. The composition of the 10% 1,3-butadiene sample was: 10% 1,3-butadiene; 29% 1-butene; 29% trans-2-butene; 12% cis-2-butene; 11% isobutylene; 4% n-butane; 4% isobutane; and 1% other.

The ACC Olefins Panel believes that conducting an OECD 422 study on a C4 stream with less than 10% 1,3-butadiene would not contribute significantly to the current understanding of the toxicology of these process streams, especially when one considers that data evaluating reproductive/developmental endpoints are or will become available for butene-1, butene-2, isobutylene, isobutane, and n-butane. Results from the OECD 422 study from a Crude 1,3-Butadiene C4 stream containing approximately ten percent 1,3-butadiene along with data on individual components will be used to read-across to the mixed C4 streams in this category for the developmental and reproductive toxicity endpoints.

The environmental endpoints were characterized by evaluating the major components of complex streams or by using the predominant component when a stream contained approximately 90% or more of a single component.

## 2 EXPOSURE AND USE

The Low 1,3-Butadiene C4 Category contains nine CAS RNs (Table 1) that are associated with the following seven process streams:

- C4 Raffinate 1
- C4 Raffinate 2
- C4 Raffinate 3

- Catalytic Butylenes
- Butane
- Butene-1
- Isobutylene

These streams are manufactured in ethylene production units (see Appendix I) and account for 100% of annual Low 1,3-Butadiene C4 stream production in the US.

The following discussion on the use of and potential exposure to streams in the Low 1,3-Butadiene C4 Category covers five of the streams in this category, which have a carbon number that is predominantly C4 and contain little or no 1,3-butadiene. The five streams include C4 Raffinate 1, C4 Raffinate 2, C4 Raffinate 3, Catalytic Butylenes, and Butene-1. The Olefins Panel also sponsors butane, which is used as a feedstock for the ethylene process and may also be isolated from the C4 raffinate streams. However, the API Petroleum HPV Testing Group has the primary HPV responsibility for butane and therefore butane is not included in this assessment. Isobutylene is also produced by the Olefins Industry, but was not included in this assessment because adequate data have been identified for this substance through the OECD SIDS HPV Program.

The category streams are high purity butene-1 and four others that are complex streams with variable compositions. The category streams are isolated intermediates that are stored in controlled on-site facilities, or isolated intermediates with controlled transport to a limited number of locations within the same company or to second parties that use the substance in a controlled way as an intermediate with well-known technology. The major applications for the category streams are:

- Alkylate feedstocks for MTBE production, which can be used as a gasoline additive
- Alkylate feedstocks for motor gasoline production
- Intermediates for plastics and other chemical production

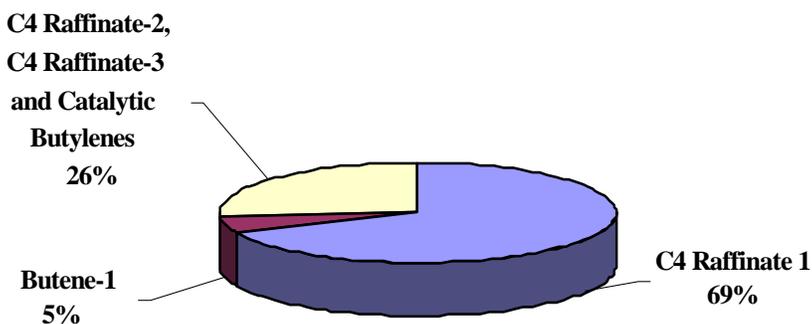
The primary category stream, C4 Raffinate 1, is derived from the Crude Butadiene C4s produced by the ethylene production process. The other category streams are separated from C4 Raffinate 1, except for the Catalytic Butylenes stream, which is a refinery process product. Butene-1, in addition to being isolated from the C4 Raffinate streams, is also produced from ethylene by the alpha olefins process. The producers of the category account for essentially all of the U.S. production of the category streams derived from Crude Butadiene C4s. The volume of catalytic butylenes produced by the Low 1,3-Butadiene C4 Category company sponsors is expected to be a low percentage of the total annual production for this stream.

There are seven CAS numbers<sup>2</sup> that are used by the Olefins Industry to represent the five category streams. Distribution of the 11 billion lbs/yr<sup>3</sup> of category production among these category streams is shown in Figure 1. This assessment does not address potential exposures within the Petroleum Industry arising from the use of the category streams. When transferred to the Petroleum Industry, these streams become only a small portion of the similar streams managed by the Petroleum Industry.

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<sup>2</sup> CAS numbers 68477-42-9, 25167-67-3, 68477-83-8, 68527-19-5, 68606-31-5, 68606-24-6 and 106-98-9.

<sup>3</sup> 11 billion lbs/yr is the total commercial production of the five category streams reported by industry participants in the Low 1,3-Butadiene Category, based on their 1998 TSCA IUR.

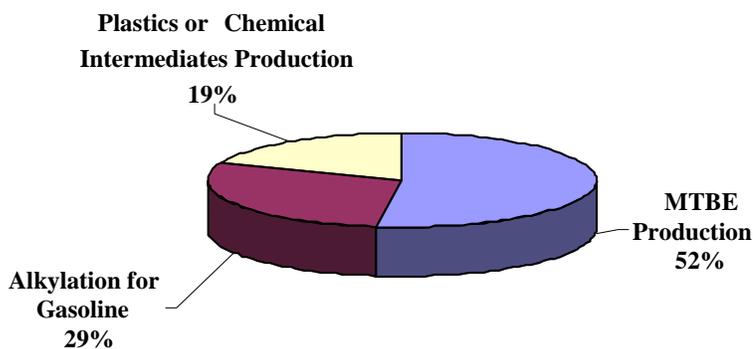
**Figure 1. Low 1,3-Butadiene C4 Category Production by Stream**

#### Storage and Transportation of Category Streams

Category streams are either used on-site where they are produced, or shipped to other industrial sites for additional processing. When shipped between industrial sites, category streams are transported as pressurized liquids in closed systems by pipeline, pressure barge, ship, tank car (rail), and tank truck (highway). Butene-1 is also distributed in some cases in pressure containers, sometimes in less than 55-gallon volumes.

#### Uses

Uses of category streams are shown in Figure 2. There are no consumer uses for these streams. Processing of the complex streams results in the consumption of the substance (as defined by CAS nomenclature) and production of a new substance(s).

**Figure 2. Uses of Low 1,3-Butadiene C4 Streams**

#### Route of Potential Exposure

Category streams are gases at ambient conditions and thus inhalation is the most likely route of exposure.

### Sources of Potential Exposure

For workers in olefins plants where the streams in this category are manufactured and used, exposure is limited because the processes use closed systems. For industrial workers at these facilities, the most likely potential for exposure will occur through inhalation of low-level concentrations in air of fugitive vapors, such as emissions from valves and pump seals; or during operations such as sampling, connecting and disconnecting bulk transportation vessels (tank cars and pressure barges), or during infrequent opening of equipment for maintenance. When loading butene-1 in containers, the vapors displaced from the containers are contained and routed to a control device or back to process and the liquid loading line is typically purged with nitrogen in order to minimize both personnel exposure and emissions.

These fugitive emissions and the other listed emission sources also result in the potential for low-level ambient air concentrations of the HPV streams at locations neighboring the industrial facilities.

The general population may be exposed to butene-1 via inhalation of ambient air, ingestion of some food oils, and use of gasoline products containing butene-1. It is a naturally occurring plant emission from mixed deciduous forests and found in the volatile organic fraction of heated soybean, rapeseed, peanut, and Canola oil. The general population may be exposed to butene-2 (a component in the complex streams) via inhalation of ambient air, handling of fuel, and exposure to engine exhaust. The general population is exposed to isobutane (a component in the complex streams) in ambient air, especially in areas of high traffic and service stations as well as by dermal contact with petroleum products. Inhalation exposure and dermal contact to isobutane may also result when using consumer products such as insect sprays, window and glass cleaners, personal spray deodorants, and rug and upholstery cleaners that contain isobutane. Occupational exposure will be by inhalation and dermal contact related to the use of fuel products and inhalation of engine exhaust.<sup>4</sup> (Butene-1 is a stream in the HPV Category, butene-2, and isobutane are components in category streams.)

### Controls Limiting Exposure

Neither OSHA (Occupational Safety and Health Administration) nor ACGIH<sup>5</sup> have established exposure limits for the streams in this category or for any of the components that are present in significant concentrations, with the exception of 1,3-butadiene. Category streams (except butene-1) contain low levels of 1,3-butadiene, typically in the range of 0.1 to 1.0%. Unless exempted, facilities that use or produce these category streams are subject to the OSHA Butadiene standard (29 CFR 1910.1051) which limits occupational 1,3-butadiene exposure to an 8-hr time-weighted-average limit of 1 ppm and a short-term (15 minutes) limit of 5 ppm.

ACGIH adopted a TLV for butane of 800 ppm, based on the effect of narcosis. Butane, which accounts for approximately 88% of the butane stream, is typically present at concentrations between 1% and 55% in the mixed category streams (C4 Raffinate 1, C4 Raffinate 2, and C4 Raffinate 3, and Catalytic Butylenes).

Among other reasons, the release of the category streams from process, storage, and transportation equipment at industrial facilities is avoided because the streams are flammable, similar in flammability and volatility characteristics to butane.

Both the U.S. EPA and state agencies enforce a wide range of volatile organic compound and hazardous air pollutant environmental regulations that control these emissions. The category

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<sup>4</sup> Hazardous Substances Databank, a database of the National Library of Medicine's TOXNET system, (<http://toxnet.nlm.nih.gov>) on November 19, 2003.

<sup>5</sup> Formerly known as the American Conference of Governmental Industrial Hygienists, now referred to only by the acronym.

streams are volatile organic compounds (VOCs) and are therefore subject to U.S. EPA and state environmental regulations that limit VOC emissions. The U.S. EPA new source performance standards of 40 CFR Part 60 may be applicable and limit VOC emissions at new or modified Olefins process units where the streams in the category are produced and used. Subpart VV of 40 CFR Part 60 limits emissions from equipment leaks, Subpart NNN limits emissions from distillation operations, and subpart RRR limits emissions from reactor systems. Facilities that produce and use the category streams are also typically subject to state operating permits and regulations that further limit VOC emissions. Butene-1 and the other C4 olefins are further regulated as a Highly Reactive VOC (HRVOC) in the Houston Galveston Area of Texas due to their contribution to ozone formation.

#### Ambient Air Concentration Data

Expected ground level concentrations of butene-1 in U.S. urban air range from 1 to 20 ppb; 6.0 vol% in exhaust of gasoline engines; 4.6 vol% as evaporate from gasoline fuel tank; and 0 to 0.3 vol% as evaporate from automobile carburetors. Ambient air concentrations (1994 through 1997) for butene-1 and selected key components in the mixed streams are available for selected industrial sites in Texas. Averages calculated from those data are shown in Table 5. Category streams account for only a portion of the measured concentrations, because these components are emitted from other sources.

**Table 5. Ambient Air Monitoring Data at Various Texas Industrial Sites (1994 through 1997) <sup>6</sup>**

Chemical	Description	Average of Annual Mean Values (ppb)	Range of Annual Mean Values (ppb)	Average of Annual 24-hr High Values (ppb)	Range of Annual 24-hr High Values (ppb)
Butene-1	Category stream	1.07	<0.01 to 6.94	7.69	<0.01 to 262.80
<i>trans</i> -Butene-2	Component in category stream	0.37	<0.01 to 3.52	2.85	<0.01 to 20.39
<i>cis</i> -Butene-2	Component in category stream	0.21	<0.01 to 1.08	1.84	0.03 to 12.84
Isobutane	Component in category stream	4.20	0.45 to 20.68	29.18	0.70 to 264.80

#### Estimates of Potentially Exposed Workers

NIOSH (NOES Survey 1981 to 1983) has statistically estimated that 545 workers (none of these are female) are potentially exposed to 1-butene in the U.S.<sup>4</sup> Butene-1 is one of the five category streams.

#### Category Emissions

Emissions from individual streams in the category or emissions of components present in significant concentrations are not included to the EPA Toxics Release Inventory (TRI)<sup>5</sup>. This

<sup>6</sup> <http://www.tnrcc.state.tx.us/air/monops/cat97/cat97.html>

inventory was established under the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) and expanded by the Pollution Prevention Act of 1990.

#### Summary of Exposure Assessment

The Low 1,3-Butadiene C4 Category includes butene-1 and four mixed C4 streams. The category mixed streams contain low levels (typically <1%) of 1,3-butadiene. The major stream in the category is C4 Raffinate 1 (69% of the production volume) and the other category streams are isolated from this stream, with the exception of catalytic butylenes (a refinery process stream). A discussion of potential for exposure to the production and use of motor gasoline streams within the petroleum refinery industry was not included in this assessment.

Category streams are either used (further processed) on site or transported in bulk to other industrial sites for processing. When transported, the category streams are moved in bulk quantities by pipeline, pressure barge, ship, tank car, and tank truck. Butene-1 is also shipped in smaller bulk containers.

All of the 11 billion pound per year production of the five category streams is consumed as chemical intermediates in other chemical manufacturing or refinery processes. There are no consumer uses of category streams. The major uses of category streams include production of the motor gasoline additive MTBE (53%), feedstock for motor gasoline production (28%), and intermediates for plastic and other chemical production (19%).

The category streams are gases at ambient conditions and inhalation is the most likely route of exposure. Category streams are produced, stored and transported in closed, pressurized systems, and therefore there is no direct worker contact with the streams. Potential for exposure of workers at the olefins process units where category streams are produced and used occurs from fugitive emission sources (equipment leaks) and from other potential emissions from the closed process. Emissions from these sources also present a potential for exposure to the environment and to areas bordering production facilities.

The general public may also be exposed to butene-1 from sources other than from category streams. Butene-1 is reported to be a naturally occurring emission from trees and found in soybean, rapeseed, peanut, and Canola oil. Some of the individual components that make up the Category streams also are present in the environment. Butene-2 and isobutane, for example are found in engine exhaust and fuels. Isobutane is used as a propellant, for example in insect sprays, deodorants, and rug and upholstery cleaners.

Neither OSHA nor ACGIH have established exposure limits for the streams in the Category or for any of the components that are present in significant concentrations, with the exception of 1,3-butadiene. Category streams (except butene-1) contain low levels of 1,3-butadiene, typically in the range of 0.1 to 5.0%. Unless exempted, facilities that use or produce these Category streams are subject to the OSHA Butadiene standard (29 CFR 1910.1051) which limits occupational exposures to 1,3-butadiene to 8-hr time-weighted-average limit of 1 ppm and a short-term (15 minutes) limit of 5 ppm.

ACGIH adopted a TLV (Threshold Limit Value) for butane of 800 ppm, based on the effect of narcosis. Butane, which accounts for approximately 88% of the butane stream, is typically present at concentrations between 1% and 55% in the mixed category streams (C4 Raffinate 1, C4 Raffinate 2, and C4 Raffinate 3, and Catalytic Butylenes). EPA and individual states enforce a number of environmental requirements intended to limit emissions of volatile organic compounds (VOC), which includes all of the category streams.

Expected ground level concentrations for butene-1 in U.S. urban air range from 1 to 20 ppb. Average annual mean value at selected industrial sites in Texas was 1.07 ppb (1994 through 1997). At the same Texas sites and time period, the average annual mean values for trans-butene-2, cis-

butene-2, and isobutane (hydrocarbon components included in the complex category streams) were 0.37, 0.21, and 4.20 ppb, respectively.

A NIOSH report estimates 545 workers were potentially exposed to butene-1 (1981 to 1983).

### **3 ENVIRONMENTAL FATE**

#### **3.1 Photodegradation**

The atmosphere is the environmental compartment of interest when considering fate processes that can impact the persistence of streams in the Low 1,3-Butadiene C4 Category because they are gaseous. Results from an environmental distribution model support the assessment that chemical constituents of these streams will partition predominantly to the air compartment. The modelling results can be largely explained by the high vapor pressure of the constituents evaluated. In spite of their water solubility, wet deposition of category constituents is not likely to play a significant role in their atmospheric fate. Constituents of streams in this category have the potential to degrade at a significant rate in the atmosphere through indirect photolytic process mediated primarily by hydroxyl radicals (OH). In comparison, direct photolysis is not expected to contribute to the degradative fate of these streams in the aqueous environment.

##### **3.1.1 Direct Photodegradation**

The direct photolysis of an organic molecule occurs when it absorbs sufficient light energy to result in a structural transformation (Harris, 1982a). The reaction process is initiated when light energy at a specific wavelength elevates a molecule to an electronically excited state. However, the excited state is competitive with various deactivation processes that can result in the return of the molecule to a non excited state.

The absorption of light in the ultra violet (UV)-visible range, 110 to 750 nm, can result in the electronic excitation of an organic molecule. Light in this range contains energy of the same order of magnitude as covalent bond dissociation energies (Harris, 1982a). Higher wavelengths (e.g. infrared) result only in vibrational and rotational transitions, which do not tend to produce structural changes to a molecule.

The stratospheric ozone layer prevents UV light of less than 290 nm from reaching the earth's surface. Therefore, only light at wavelengths between 290 and 750 nm can result in photochemical transformations in the environment (Harris, 1982a). Although the absorption of UV light in the 290-750 nm range is necessary, it is not always sufficient for a chemical to undergo photochemical degradation. Energy may be re-emitted from an excited molecule by mechanisms other than chemical transformation, resulting in no change to the parent molecule.

A conservative approach to estimating a photochemical degradation rate is to assume that degradation will occur in proportion to the amount of light at wavelengths >290 nm absorbed by the molecule (Zepp and Cline, 1977). Saturated hydrocarbons do not absorb light above 200 nm. Characteristic absorbance maxima ( $\lambda_{\text{max}}$ ) and associated molar absorptivities ( $\epsilon$ ) for two unsaturated hydrocarbons, including 1,3-butadiene, are listed in Table 6 (Harris, 1982a).

**Table 6. Characteristic Absorbance Maxima ( $\lambda_{\max}$ ) and Associated Molar Absorptivities ( $\epsilon$ ) for Two Unsaturated Hydrocarbons from Streams in the Low 1,3-Butadiene C4 Category**

Hydrocarbon	$\lambda$ below 290 nm	
	$\lambda_{\max}^*$	$\epsilon$
Ethylene	193	10,000
1,3-Butadiene	217	20,900

\* Values developed in organic solvents and regarded as approximate absorption maxima in aqueous solution.

Olefins with one double bond, two conjugated double bonds, or multiple un-conjugated bonds, which constitute the majority of the chemicals in the Low 1,3-Butadiene C4 Category, do not absorb appreciable light energy above 290 nm. Streams in this category do not contain constituent molecules of significant concentration that will undergo direct photolysis. Therefore, this fate process will not contribute to a measurable degradative removal of chemical constituents in this category from the environment.

### 3.1.2 Indirect Photodegradation

In the environment, organic chemicals emitted into the troposphere are degraded by several important transformation processes. The dominant transformation process for most compounds is the daylight reaction with hydroxyl ( $\text{OH}^\cdot$ ) radicals (Atkinson, 1988; Atkinson, 1989). The rate at which an organic compound reacts with  $\text{OH}^\cdot$  radicals is a direct measure of its atmospheric persistence (Meylan and Howard, 1993).

AOPWIN estimates the rate constant for the atmospheric, gas-phase reaction between photochemically produced hydroxyl radicals and organic chemicals. The rate constants estimated by the program are then used to calculate atmospheric half-lives for organic compounds based upon an average atmospheric concentration of hydroxyl radicals.

Since the reactions necessary for this degradative process only take place in the presence of sunlight, the atmospheric half-lives are normalized for a 12-hour day. The seven chemicals selected to represent the atmospheric half-life range of streams in this category are C4 hydrocarbons that are predominant among the nine CAS RNs (Table 7).

**Table 7. Hydroxyl Radical Photodegradation Half-life of Selected Chemicals from Streams in the Low 1,3-Butadiene C4 Category**

Chemical	Calculated Half-Life* (hrs)	$\text{OH}^\cdot$ Rate Constant ( $\text{cm}^3/\text{molecule}\cdot\text{sec}$ )
Isobutane	52.6	2.4 E-12
n-Butane	48.8	2.6 E-12
Isobutylene	2.5	51.7 E-12
Cis-Butene-2	2.3	56.7 E-12
Trans-Butene-2	3.0	64.3 E-12
Butene-1	4.7	27.4 E-12
1,3-Butadiene	1.9	66.6 E-12

\* Atmospheric half-life values are based on a 12-hr day and an  $\text{OH}^\cdot$  concentration of  $1.5\text{E}6$ , which is the default concentration used by the model.

Atmospheric oxidation via hydroxyl radical attack can be a significant route of degradation for streams in this category. Based on calculated values, streams in this category can have an atmospheric half-life range of 1.9 to 52.6 hours as a result of indirect photolysis by hydroxyl radical attack.

### 3.2 Stability in Water (Hydrolysis)

Hydrolysis of an organic molecule occurs when a molecule (R-X) reacts with water (H<sub>2</sub>O) to form a new carbon-oxygen bond after the carbon-X bond is cleaved (Gould, 1959; Harris, 1982b). Mechanistically, this reaction is referred to as a nucleophilic substitution reaction, where X is the leaving group being replaced by the incoming nucleophilic oxygen from the water molecule. The leaving group, X, must be a molecule other than carbon because for hydrolysis to occur, the R-X bond cannot be a carbon-carbon bond.

The carbon atom lacks sufficient electronegativity to be a good leaving group and carbon-carbon bonds are too stable (high bond energy) to be cleaved by nucleophilic substitution. Thus, hydrocarbons, including alkenes, are not subject to hydrolysis (Harris, 1982b) and this fate process will not contribute to the degradative loss of chemical constituents in this category from the environment.

Under strongly acidic conditions the carbon-carbon double bond found in alkenes, such as those in the Low 1,3-Butadiene C4 Category, will react with water by an addition reaction mechanism (Gould, 1959). The reaction product is an alcohol. This reaction is not considered to be hydrolysis because the carbon-carbon linkage is not cleaved and because the reaction is freely reversible (Harris, 1982b).

Chemicals that have a potential to hydrolyze include alkyl halides, amides, carbamates, carboxylic acid esters and lactones, epoxides, phosphate esters, and sulfonic acid esters (Neely, 1985). The chemicals in this category are primarily olefins that contain at least one double bond (alkenes). The majority of the remaining chemicals are saturated hydrocarbons (alkanes). These two groups of chemicals contain only carbon and hydrogen. As such, their molecular structure is not subject to the hydrolytic mechanism described above. Therefore, chemicals in the Low 1,3-Butadiene C4 Category have a very low potential to hydrolyze, and this degradative process will not contribute to their removal in the environment.

### 3.3 Distribution in the Environment

Fugacity-based multimedia modeling provides basic information on the relative distribution of a chemical between selected environmental compartments, which can include air, soil, water, sediment, suspended sediment, and biota. A widely used fugacity model, the EQC (Equilibrium Criterion) Level I model (Mackay *et al.*, 1996; Mackay, 1998) calculates chemical distribution between these compartments based on the input of basic physicochemical parameters including molecular weight, water solubility, log P<sub>ow</sub>, and melting point.

Results of the EQC Level I model (Table 8) for selected chemical constituents of streams from this category suggest that they will partition primarily to air, with a small percentage partitioning to water. These results can be explained by their high vapor pressure. Distribution of these chemicals to each remaining compartment (soil, sediment, suspended sediment, biota) is calculated as less than 0.01%.

**Table 8. Environmental Distribution as Calculated by the EQC Level I Fugacity Model for Selected Chemicals from Streams in the Low 1,3-Butadiene C4 Category**

Chemical	Distribution Per Environmental Compartment (%)					
	Air	Water	Soil	Sediment	Suspended Sediment	Biota
Isobutane	99.99	0.01	<0.01	<0.01	<0.01	<0.01
n-Butane	99.99	0.01	<0.01	<0.01	<0.01	<0.01
Isobutylene	99.99	0.01	<0.01	<0.01	<0.01	<0.01
cis-Butene-2	99.98	0.02	<0.01	<0.01	<0.01	<0.01
trans-Butene-2	99.98	0.02	<0.01	<0.01	<0.01	<0.01
Butene-1	99.99	0.01	<0.01	<0.01	<0.01	<0.01
1,2-Butadiene	99.96	0.04	<0.01	<0.01	<0.01	<0.01
1,3-Butadiene	99.97	0.03	<0.01	<0.01	<0.01	<0.01

Note: The distribution values were determined using physical property data from the EPIWIN (1999) database.

The seven chemicals selected to characterize the transport/distribution range are C4 hydrocarbons that are predominant across the streams in this category. Physical property data (Table 4) used in the model are from the EPIWIN (1999) database.

### 3.4 Biodegradation

Biodegradation is the use of a chemical by microorganisms as a source of energy and carbon. The parent chemical is broken down to simpler, smaller chemicals, which can be eventually converted to inorganic forms such as carbon dioxide, nitrate, sulfate, and water, depending on the composition of the parent chemical.

The microbial metabolism of aliphatic alkenes can be initiated by attack at the double bond (Watkinson and Morgan, 1990). Four degradative processes have been identified:

- Oxygenase attack upon a terminal methyl group to the corresponding alcohol, aldehyde, and acid
- Subterminal carbon oxygenase attack to the corresponding alcohol and ketone
- Oxidation across the double bond to the corresponding epoxide
- Oxidation across the double bond to the corresponding diol

Streams in the Low 1,3-Butadiene C4 Category are gaseous hydrocarbons, composed predominantly of chemicals with carbon numbers smaller than C5.

Constituent chemicals from the two process streams in this category are simple hydrocarbons (Table 2), the majority of which are calculated to partition primarily to the air where physical processes will contribute to their rapid degradation (see [Indirect Photodegradation](#) above for specific degradation rates of selected chemicals from this category). Consequently, their availability to microbial degraders can be significantly limited. Because of the partitioning behavior of chemicals in this category, biodegradative processes will be less likely to contribute to their loss from the environment.

Streams from the Low 1,3-Butadiene C4 Category do not lend themselves to being evaluated for biodegradability using standard experimental designs because of their physical state. However, there is microbial metabolism information for several of the unsaturated C4 constituents in this

category, including 1,3-butadiene, which demonstrates they have the potential to biodegrade. The sections immediately below summarize results of studies for selected constituents from this category. The data do not allow for an estimation of the extent of biodegradability relative to a standard 28-day test procedure using a microbial inoculum from a wastewater treatment facility. However, the constituents discussed below are predicted by BIOWIN, Biodegradation Probability Program (EPIWIN, 1999), as having the potential to biodegrade rapidly. [BIOWIN is a model in EPIWIN that calculates the probability of an organic chemical to rapidly biodegrade by a mixed population of microorganisms. BIOWIN can also estimate the time required to meet primary and ultimate biodegradation criteria.]

### 3.4.1 Propylene Biodegradation

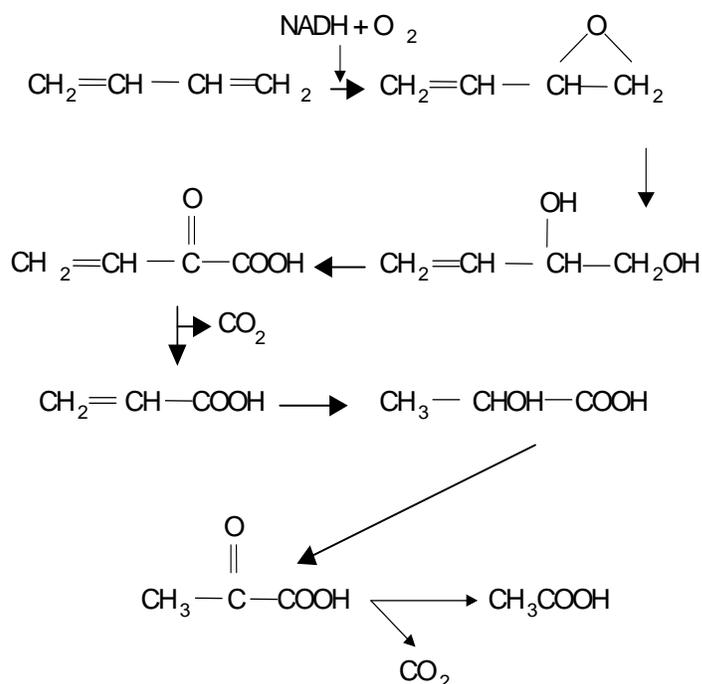
Propylene has been shown to be a growth substrate for several microorganisms. Isolated bacterial strains with a potential to biodegrade propylene under aerobic conditions were identified from the genus *Nocardia*, *Mycobacterium*, and *Xanthobacter* (de Bont *et al.*, 1980; de Bont *et al.*, 1982; de Bont *et al.*, 1983; van Ginkel and de Bont, 1986). Other species from the genus *Pseudomonas* and *Aerobacter* that were isolated from soil have also been associated with the ability to aerobically degrade propylene after they were shown to metabolize propylene oxide (Raja, 1991), an intermediate in the propylene metabolic pathway (van Agteren *et al.*, 1998).

Two pathways for the aerobic metabolism of propylene have been described (van Agteren *et al.*, 1998) that include the formation of either 1,2-propanediol or acetyl CoA prior to mineralization to CO<sub>2</sub>.

### 3.4.2 1,3-Butadiene Biodegradation

Experimental studies to determine a catabolic pathway for 1,3-butadiene as mediated by a *Nocardia sp.* (Watkinson and Somerville, 1976) resulted in the series of reactions shown in Figure 3.

**Figure 3. Proposed Microbial Metabolic Pathway for the Degradation of 1,3-Butadiene by a *Nocardia sp.***



The intermediary metabolic steps depicted in Figure 3 result in the production of acetic acid (CH<sub>3</sub>COOH) which can be further metabolized. In addition, 1,3-butadiene has been estimated to have an aerobic aquatic biodegradation half-life ranging from 1 to 4 weeks (Howard *et al.*, 1991).

### 3.4.3 1-Butene Biodegradation

Isolated bacterial strains have been evaluated for their potential to biodegrade 1-butene under aerobic conditions. Bacteria from two genus, *Mycobacterium* spp. and *Xanthobacter* spp., isolated from environmental samples have demonstrated the ability to degrade 1-butene (Hou *et al.*, 1983; Habets-Crützen *et al.*, 1984; van Ginkel and de Bont, 1986; Weijers *et al.*, 1995). Epoxybutane was shown to be converted to the corresponding ketone using a cell extract from a *Xanthobacter* spp. (Weijers *et al.*, 1995). These studies suggest that 1-butene can be biodegraded and that microbial metabolism can contribute to the overall loss of this chemical from the environment.

### 3.4.4 2-Butene Biodegradation

Although, 2-butene has not been reported as a microbial growth substrate, an isolated bacterial strain, *Xanthobacter* spp., was evaluated for its potential to biodegrade various epoxyalkanes. Both diastereomeric forms of 2,3-epoxybutane were shown to degrade with degradation rates of 6 and 9 nmol/min/mg protein for trans- and cis- geometric isomers, respectively (Weijers *et al.*, 1988). These data suggest that a metabolic pathway is present in bacteria that will degrade these alkenes.

### 3.4.5 Isobutylene Biodegradation

Although, isobutylene has not been reported as a growth substrate for bacteria, isolated bacterial strains have been evaluated for their potential to biodegrade 1-butene under aerobic conditions. Epoxybutane was converted to the corresponding ketone using a cell extract from a *Xanthobacter* spp. (Weijers *et al.*, 1995). In the same study, 2-methyl-1,2-epoxypropane was not converted suggesting that isobutylene metabolism is not mediated in a manner similar to 1-butene by this organism. However, because of the structural similarity between 1-butene and isobutylene, isobutylene biodegradation may occur through a process not yet evaluated.

### 3.4.6 Abiotic and Biotic Degradation Summary

The stream constituents from this category will partition primarily to the air where physical degradative processes will dominate their fate. Data show that these chemicals are subject to rapid physical degradation. Selected constituents have also been shown to be subject to biodegradation. Overall, the constituent chemicals and consequently the streams from this category are expected to degrade rapidly in the environment from physical processes and not persist.

## 4 HUMAN HEALTH HAZARDS

Seven streams comprise the Low 1,3-Butadiene C4 Category. The major components of these streams are butanes and monobutenes. Butanes are being evaluated as part of the Petroleum HPV Test Group. Existing data included in the Petroleum Gases Test Plan for butane and isobutene are summarized in this report for completeness. However, robust summaries will not be included as they will be submitted under the API Petroleum HPV Testing Groups test program. Available health effects data on butenes, isobutylene, 1-butene and 2-butene, are summarized in this document. 1,3-Butadiene is a minor constituent of these streams ranging from 0 to 5%. Streams containing higher 1,3-butadiene concentrations were addressed in the Crude Butadiene C4 Category Summary. Some data from the Crude Butadiene C4 Category are utilized in this report where data were unavailable or to augment conclusions derived from available data on butenes.

## 4.1 Effects on Human Health

### 4.1.1 Acute Toxicity

Acute toxicity of the Low 1,3-Butadiene C4 Category can be estimated with available data. Data exist for several components of the streams that comprise this category. As the streams are gaseous at room temperature, data are from inhalation toxicity studies (Table 9).

**Table 9. Summary of Acute Inhalation Toxicity Data for the Low 1,3-Butadiene C4 Category**

CAS RN and Chemical Name	Test Organism	Exposure Duration (hr)	Concentration Inducing Respiratory Arrest (ppm)
107-01-7 2-Butene (racemic)	Rat	4	>10,000*
75-28-5 Isobutane	Rat	0.25	>570,000*
106-97-8 n-butane	Rat	4	276,000*
115-11-7 Isobutylene	Mouse	0.33	320,000
106-98-9 1-Butene	Mouse	0.33	272,000
107-01-7 2-Butene ( <i>cis</i> )	Mouse	0.33	255,000
107-01-7 2-Butene ( <i>trans</i> )	Mouse	0.33	211,000

\* LC<sub>50</sub> study

#### Studies in Animals

##### *Inhalation*

In a well conducted and reported acute toxicity study, five male and female Wistar rats (CrI:WI(WU)BR) were exposed to a racemic mixture 2-butene (95% purity, 42.4% *cis*, 55.3% *trans*) at a limit concentration of 23.1 g/m<sup>3</sup> (approximately 10,000 ppm) for 4 hr (Arts, 1992). Filtered air was used as the control. Chamber concentrations were monitored by FID. Following exposure, rats were housed in individual cages for 14 days of observations. Body weights were measured prior to exposure and on post exposure days 7 and 14. Clinical signs were evaluated during and following exposure and once daily during the 14-day observation period. Following the observation period, gross pathological observations were conducted at necropsy. No mortality was observed during the study. Restlessness was observed during and after exposures on the first day. No clinical signs were observed in the 14-day observation period. No change in body weight was observed and no adverse effects were noted at necropsy. The LC<sub>50</sub> is greater than 10,000 ppm.

Lethality of isobutylene, 1-butene, 2-butene (*cis*) and 2-butene (*trans*) was examined during an evaluation of the relationship between anaesthesia and respiratory arrest of unsaturated hydrocarbons and carbon oxygen ring compounds. Mice (sex and strain not specified) were exposed to concentrations of these compounds that produced anaesthesia in 10 minutes. Mice were exposed to test compound in a large jar equipped with an apparatus to introduce oxygen or test compound. Concentrations that produced anaesthesia or respiratory arrest were recorded. Exposures were

terminated after 20 minutes. Concentrations that induced respiratory arrest in mice were 32% (320,000 ppm), 27.2% (272,000 ppm), 25.5% (255,000 ppm) and 21.1% (211,000 ppm) for isobutylene, 1-butene, 2-butene (*cis*) and 2-butene (*trans*), respectively (Virtue, 1950). Isobutane was evaluated for potential central nervous system (CNS) effects in rats after a 15-minute exposure period. EC<sub>50</sub> for CNS effects was calculated as was the LC<sub>50</sub> value. The EC<sub>50</sub> (CNS stimulation) was 200,000 ppm after 10 minutes and the LC<sub>50</sub> (15-minutes) was 570,000 (API 2000). A LC<sub>50</sub> value of 276,000 ppm was reported for butane in a poorly described study (API 2000).

#### Conclusion

Although only 2-butene has been evaluated in a guideline acute toxicity study, available data adequately address the acute lethality of Low 1,3-Butadiene C4 Category. The LC<sub>50</sub> for 2-butene is greater than 10,000 ppm, the limit dose, indicating a low order of toxicity. Studies in mice were conducted that evaluated the relationship between lethality and anesthesia for the major components of the streams in this category, isobutylene, 1-butene, and 2-butene (*cis* and *trans*). In addition, isobutane and butane have also been evaluated in acute toxicity studies. While study details are limited, results are consistent with other C4 acute toxicity studies. Results indicate that 2-butene is the most potent material, inducing respiratory arrest at a concentration of 211,000 ppm in twenty minutes. As 2-butene is the most potent for inducing respiratory arrest, it is reasonable to use the results from the acute lethality test as a surrogate for the streams in this category.

#### **4.1.2 Irritation**

No skin or eye irritation data exist for streams of the Low 1,3-Butadiene C4 Category. Data are available for Crude Butadiene C4 Category. These data are considered applicable to the Low 1,3-Butadiene C4 Category.

#### Studies in Animals

##### *Skin Irritation*

In an irritation screening study, 0.1 ml of butadiene concentrate (CAS# 68955-28-2: 67% 1,3-butadiene; 30% butenes; and 2% 1,2-butadiene) was applied to the skin of one male and one female rabbit New Zealand White rabbit (Mobil Environmental and Health Science Laboratory, 1985). The application site was occluded with a rubber dam. No irritation was observed at 1, 3, or 7 days after dosing.

##### *Eye Irritation*

In an irritation screening study, 0.1 ml of butadiene concentrate (CAS# 68955-28-2: 67% 1,3-butadiene; 30% butenes; and 2% 1,2-butadiene) was applied to the eye of one male and one female rabbit (Mobil Environmental and Health Science Laboratory, 1985a). Test stream was stored on dry ice prior to administration. No irritation was observed at 1, 3, or 7 days after dosing.

#### Conclusion

Butadiene concentrate is non-irritating to rabbit skin and eyes. Lack of irritation may be due to non-irritating properties of the test stream or rapid removal of test stream from the application site by evaporation. Low 1,3-Butadiene C4 streams possess these same properties and as such, these data are considered applicable.

#### **4.1.3 Repeated Dose Toxicity**

Repeated dose toxicity tests have been conducted on a variety of the components identified in this category (Table 10). These studies range from 28 to 90 days in duration and have been conducted in rats and mice.

**Table 10. Summary of Repeated Dose Toxicity Data for the Low 1,3-Butadiene C4 Category**

CAS RN and Chemical Name	Test Organism	Exposure Duration (days)	NOAEL
<b>Inhalation (ppm)</b>			
115-11-7 Isobutylene (>99%)	Sprague-Dawley	90	8,000
106-98-9 1-Butene (>99%)	Crl:CD Rat	28	8,000
107-01-7 2-Butene, racemic (95%)	Wistar Rat	39 to 46	2,500
68476-52-8 C4 Crude Butadiene (10)	Crl:CD Rat	36	>20,000 mg/m <sup>3</sup>
<b>Oral (mg/kg/day)</b>			
115-11-7 Isobutylene (>99%)	Sprague-Dawley	28	14.86

Studies in Animals*Inhalation*

In a ninety-day repeat dose study, groups of 10 male and 10 female Sprague-Dawley rats were exposed to 0; 250; 1,000; or 8,000 ppm, isobutylene (>99.7% purity). Exposures were conducted for 6 hr/day, 5 day/week for 13 weeks (Blackett, 1982). Body weights and food consumption were recorded weekly. Blood was collected from rats at study initiation, week five and terminal sacrifice (week 13). Urine samples were collected at week 13. Organ weights were determined for select organs with histopathology conducted on control and high exposure animals. No biologically significant treatment related effects were observed at any dose level. Elevated ketones were detected in urine in the mid and high dose groups. The significance of this effect is unknown and may be due to metabolism of the test compound to ketones. The NOAEL in this study was determined to be 8,000 ppm.

Effects of repeated exposure to 1-butene (>99% purity) were evaluated as part of an OECD 422, Repeated Exposure Reproductive/Developmental Toxicity Screen in Crl:CD rats (Hoffman, 2003). Twelve male and female rats were exposed to concentrations 0; 500; 2,000; or 8,000 ppm (0; 524; 2,062; and 8,271 ppm actual) 1-butene for 28 days, 6 hours/day, and 7 days/week (this study contained an additional group of twelve female rats for reproductive evaluation). Males and females were sacrificed at the end of exposure. Effects on general toxicity, neurobehavioral activity, clinical chemistry, and hematology were evaluated. At necropsy, organs were weighed, evaluated grossly and histopathological evaluation was conducted. No deaths or treatment related clinical observations were reported. No treatment related changes were observed in body weight, weight changes, food consumption, motor activity, functional observational battery parameters, hematology, prothrombin time, clinical chemistry, organ weights, or gross pathology. There was a slight increase, with no clear exposure response relationship, in the incidence and severity of mixed inflammatory cells in the cecal mucosa of rats exposed to 1-butene at exposure levels of 2,000 ppm and above. This finding was also present in the control group. As such, this finding was considered fortuitous and unlikely related to treatment. The NOAEL in this study was 8,000 ppm.

As part of an OECD 422 Combined repeated dose toxicity and reproductive developmental toxicity test, 12 male and female Wistar rats were exposed to 0; 2,500; or 5,000 ppm 2-butene (*cis* and *trans*, 95% purity) for 6 hours/day, 7 days/week (Waalkens-Brendsen and Arts, 1992). Males were exposed for 39 to 46 days; females were exposed two weeks prior to mating and through mating to gestation day 19. Body weights and food consumption were recorded. At study termination, blood was collected for clinical chemistry and hematology. Organs were weighed, and processed for microscopic examination. Control and high dose organs were examined microscopically. Body weight change was lower for male rats in the first and fourth week of exposure in the 2,500 ppm group and in the first week in the 5,000 ppm group. Female body weights were reduced in the 2,500 (14 days of exposure) and 5,000 (7 and 14 days exposure) ppm groups. Female body weights were comparable during mating and gestation, but were reduced in the 5,000 ppm group on lactation day 1. Male rats in both exposure groups had increased total white cell and lymphocyte counts, however, there was no dose-response and counts were within the historical control range. A decrease in plasma calcium concentration was observed in high dose males. No other adverse treatment related effects were observed. The NOAEL for this study was 2,500 ppm.

Effects of repeated exposure to C4 Crude Butadiene (CAS# 68476-52-8: 10% 1,3-butadiene; 4% isobutane; 29% *trans*-2-butene; 29% 1-butene; 11% isobutylene; and 12% *cis*-2-butene) were evaluated as part of an OECD 422, Repeated Exposure Reproductive/Developmental Toxicity Screen in Crl:CD rats (Carney *et al.*, 2001). Twelve male and female rats were exposed to vapor concentrations 0; 2,000; 10,000; or 20,000 mg/m<sup>3</sup> Crude Butadiene for 36 or 37 days, 6 hr/day, 7 day/week (this study contained an additional group of twelve female rats for reproductive and developmental toxicity screening evaluation). Males and females were sacrificed at the end of exposure. Effects on general toxicity, neurobehavioral activity, clinical chemistry, and hematology were evaluated. At necropsy, organs were weighed, evaluated grossly and histopathological evaluation was conducted. No deaths or treatment related clinical observations were reported. No treatment related changes were observed in body weight, sensory evaluation, rectal temperature, fore/hindlimb grip performance, motor activity total counts, hematology, prothrombin time, clinical chemistry, organ weights, gross pathology, or histopathology. In evaluation of motor activity, the treatment-by-time-by-epoch interaction was significant. However, further evaluation indicated that this difference could be attributed to the time by epoch interaction rather than a treatment related effect. Females in the 2,000 mg/m<sup>3</sup> dose group had an increased hematocrit and a decrease in serum protein. However, these effects did not demonstrate a dose response and were not observed in males at the same dose level. As such these findings were considered incidental and not indicative of a treatment related response. The NOAEL in this study was 20,000 mg/m<sup>3</sup>.

#### *Oral*

Groups of five male and five female Sprague-Dawley rats were administered isobutylene (99.7%) by gavage once a day, 7 days/week for four weeks (Jones, 1986). Isobutylene was dissolved in corn oil and administered at dose levels of 0, 1.49, 14.86, and 148.55 mg/kg/day. Rats were examined daily for morbidity and mortality; body weights were recorded weekly. At terminal sacrifice, blood was collected for hematology and clinical chemistry, gross necropsy was conducted and tissues collected and preserved for histopathological examination. A reduction in white blood cell count, primarily in total leukocytes and monocytes, was observed in high dose males and females. No other treatment related changes were noted. The NOEL in this study was 14.86 mg/kg/day.

#### Conclusion

Data are available to adequately characterize the repeated dose toxicity of Low 1,3-Butadiene C4 Category. Repeat dose studies have been conducted on most of the individual components of the streams that comprise this category. The data are consistent in that they demonstrate minimal effects in rats with the exception of body weight changes following repeated exposures. Other effects observed were generally not dose related or were within the range of historical controls. The

repeat dose toxicity of these components, and by analogy streams, is not remarkable. Repeat dose studies were not available for butane or isobutene at the time this report was written. However, repeat dose study results will become available as part of the API Petroleum HPV Testing Group test plan on petroleum gasses. It is anticipated that results from repeat dose studies on butane and isobutene will be consistent with results presented in this report on other C4s. If results are different this category report will be re-evaluated.

#### 4.1.4 Mutagenicity

Genetic toxicity has been evaluated both *in vitro* and *in vivo* assays on the major components of Low 1,3-Butadiene C4 streams. *In vitro* assays include Ames *Salmonella* Reverse Mutation assay, chromosomal aberrations, mammalian cell transformation assay, and mouse lymphoma assay. Potential for the *in vivo* induction of chromosomal aberrations has been examined in mice following inhalation exposure.

##### Studies in Animals

###### *In vitro* Studies

Mutagenic activity of isobutylene (99.8%, liquified) was evaluated in the Ames *Salmonella* Reverse Mutation assay (MacGregor *et al.*, 1981). *Salmonella typhimurium* tester strains TA 98, TA 100, and TA 1535, TA 1537, TA 1538 and *E. coli* WP 2uvrA(pKM101) were overlaid on agar with or without rat S9 activation system. Exposure to isobutylene was accomplished by inverting the plates containing media, bacteria and S9 (if included) over jars containing known quantities of isobutylene for 48 hours. Concentration of isobutylene in the jars was achieved by metering the flow of isobutylene and hydrocarbon free air into the 6.25-liter jar. For the initial trial, duplicate plates were exposed to concentrations of 5, 10, 20, 30, 40, and 50%; in the second trial, a single plate was exposed to concentrations of 10, 20, 40, 60, 80, and 100% isobutylene. Positive controls consisted of 4-actyl aminoflourene, and methyl methane sulfonate, applied in liquid, and vinyl chloride (30%) administered as gas in the system described above. Positive controls responded appropriately, inducing from 3 to 30 fold increases above negative controls. Exposure to isobutylene did not induce mutagenic activity at any exposure concentration in any strain. Toxicity was observed both with and without activation at concentrations of 80 and 100% isobutylene.

Isobutylene was administered to mouse lymphoma L5178Y cells with and without rat liver S9 metabolic activation to assess mutagenic activity (MacGregor and Ross, 1981). Mouse lymphoma cells were exposed to airborne isobutylene concentrations ranging from 6.25 to 100%. Exposure atmospheres were generated by mixing isobutylene and filtered air in mixing chamber prior to delivery into incubation jars. Cells were exposed for 24 hours to isobutylene. Ethyl methane sulfonate (without S9) and acetyl amino fluorine (with S9) were used as positive controls. Low cell survival was noted in cultures with and without S9 activation. Increased cell survival was achieved by addition of extra washing steps (with and without S9) and reduction of exposure time (with S9). Cell survival increased in subsequent trials. Mutant frequencies were similar in isobutylene-treated and control cultures with and without S9 activation. Appropriate increases were observed in cultures treated with positive controls. Isobutylene showed no evidence of mutagenic activity in the mouse lymphoma assay.

Transformation of mouse embryo fibroblast derived cells was examined following exposure to isobutylene (MacGregor and Poole, 1981). For a toxicity assessment, flasks containing cultured cells were placed in 6.25 l incubation jars containing concentrations of isobutylene ranging from 6.25 to 100%. These concentrations were achieved by combining isobutylene and 5% CO<sub>2</sub> air in a mixing chamber and then filling the 6.25 l incubation jars. Exposure continued for 24 hours, followed by replacement of medium and additional incubation for three weeks. For the transformation assay, exposures were conducted in a similar manner with the exceptions being that the exposure concentrations were 0, 25, 50 and 100% isobutylene, S9 was added to half the flasks

for metabolic activation and the cells were maintained for eight days. Isobutylene did not transform cultured mouse fibroblast cells in the presence or absence of metabolic activation.

Mutagenicity of 1-butene was examined in *Salmonella typhimurium* strains TA 97, TA98, and TA100 with or without metabolic activation by rat or hamster liver S9 fractions. 1-Butene was prepared for testing by diffusion into ethanol at 0°C. Test concentrations of 0, 1.3, 4.2, 13.0, 43.2, or 130 µg/plate were limited by solubility of 1-butene in ethanol. Positive controls were sodium azide (TA100), 9-aminacridine (TA97), 2-nitrofluorene (TA98) for non-activated tests, and 2-aminoanthracene for all S9 assays. 1-Butene did not induce an increase in revertant colonies at any dose level in this assay.

*Salmonella typhimurium* strains TA 98, TA100, TA 1535, and TA 1537 and *E. coli* WP2 urv A were exposed to either 1-butene or 2-butene for assessment of mutagenicity (Araki *et al.*, 1994). Exposure was achieved by generating a 50% atmosphere and pumping that atmosphere in a 10 l gas sampling bag containing plates with bacteria and media for 24 hours. At the end of exposure, the exposure atmosphere was removed and replaced by sterile air. Several other gases were tested at the same time including 1,3-butadiene. Neither 50% 1-butene nor 50% 2-butene increased the revertant frequency compared to controls. In contrast, an increase in revertant frequencies was observed for 1,3-butadiene.

2-Butene was evaluated for mutagenic effects in an OECD Guideline 471 Reverse Mutation in Bacteria test (Thompson, 1992). *Salmonella typhimurium* strains TA 98, TA 100, TA 1535, and TA 1537 were exposed to concentrations of 0, 10, 20, 40, 60, and 80% 2-butene. Atmospheres were generated by mixing 2-butene and filtered air. Plates containing bacteria, agar and rat liver S9 or phosphate buffer were covered with a triple vented lid and exposed to 2-butene concentrations in a 10 stainless steel container for 48 hours. Positive controls without activation were N-ethyl-N' nitro-N-nitrosoguanidine (TA 100, TA 1535), 9 amino-acridine (TA 1537), 4-nitroquinoline-1-oxide (TA 98). For plates containing S9 fractions, 2-aminoanthracene (TA 1535) and benzo(a)pyrene (all other strains) were used as positive controls. Toxicity was observed in all strains at 80% 2-butene; slight toxicity was observed at 60% 2-butene. No significant increases in number of revertant frequencies of any strain were observed at any dose concentration with or without S9 activation. 2-Butene was not active in the bacterial reverse mutation assay.

The ability of 2-butene to induce chromosomal aberrations was examined in primary rat blood lymphocyte cultures under the OECD Guideline 473, Chromosome Aberrations in Mammalian Cells (Wright, 1992). Primary rat lymphocytes were obtained from male Sprague-Dawley rats and grown in culture for 48 hours prior to exposure to 2-butene. Cells were exposed to atmospheres of 0, 10, 20, 40, 50, 60, 80, or 100% 2-butene in sealed flasks repeatedly shaken for 4 hours (cultured with S9) or 16 hours (cultured without S9). Atmospheres were generated from mixing 2-butene and clean filter air using precalibrated gas flow meters and delivery of the mixture into a culture flask. Cells incubated with S9 fraction had either a 16 hr (20 hours total) or 26 hr (30 hours total) recovery period. Positive controls included ethyl methyl sulfonate (without S9), cyclophosphamide (with S9), and vinyl chloride (administered as a gas for both with and without S9). Toxicity was observed at concentrations greater than 50% with S9 as indicated by hemolysis. A dose-related reduction in mitotic indices was observed with and without metabolic activation. No significant increase in frequency of structural chromosome aberrations or polyploid cells was observed at any concentration.

The mutagenicity of butane and isobutane have been evaluated in *Salmonella typhimurium* strains TA 98, TA 100, TA1535, TA1537 and TA1538 with (rat liver S9 fractions) and without metabolic activation (API 2000). *Salmonella typhimurium* strains were exposed to gas concentrations of 10, 20, 30, 40, or 50% in air for six hours. Methylene chloride was used as a positive control. The positive control was mutagenic in strains TA98 and TA100, and slightly mutagenic in TA1535. Neither butane nor isobutene were toxic or mutagenic at any of the concentrations tested.

*In vivo Studies*

Ten male B6C3F1 mice were exposed to concentration of 0; 1,000; 3,260; or 10,000 ppm isobutylene by inhalation for two days, 6 hours/day (Przygoda, 1990). Exposure concentrations were confirmed by online gas chromatography. Twenty-four hours following the final exposure, femoral bone marrow was collected to evaluate micronuclei formation in polychromatic erythrocytes. 1,3-Butadiene (1,000 ppm) was used as the positive control. Isobutylene did not induce a statistically significant increase nor a dose related increase in the number of micronuclei in mouse bone marrow polychromatic erythrocytes (PCEs). An increased percentage of PCEs was observed, however this effect was within historical values and is not considered biologically significant. 1,3-Butadiene induced statistically significant increases in micronuclei and a reduced percent PCE, indicative of toxicity. Isobutylene was not clastogenic in mouse bone marrow under conditions of this test.

Ten male and female Crl:CD-1 BR Swiss mice were exposed to 0; 1,000; 9,000; or 22,000 ppm 1-butene via inhalation for 2 hours/day, for 2 consecutive days (Khan and Ward, 1985). Five mice per sex per dose were sacrificed on days 3 and 4 (24 and 48 hours post-exposure), and bone marrow smears prepared. Two daily ip injections of cyclophosphamide (75 mg/kg) were administered to the positive control group. Loss of consciousness was observed in mice during exposures; no other adverse effects were observed. No significant increase in micronuclei formation was observed in 1-butene exposed mice.

Conclusion

Adequate data are available to evaluate the genotoxicity of Low 1,3-Butadiene C4 streams. These data include examination of the major reactive constituents of the streams comprising this category, butenes, in mutagenicity, transformation and clastogenicity assays. Isobutylene, 1-butene, 2-butene (*cis* and *trans*), butane, and isobutane were negative in bacterial reverse mutation assays. Further, no chromosomal aberrations were observed following *in vitro* exposure to 2-butene, and *in vivo* exposures of isobutylene and 1-butene. As such, it can be concluded that the streams in this category are not genotoxic.

**4.1.7 Toxicity for Reproduction**

Reproductive and developmental toxicity of the Low 1,3-Butadiene C4 Category was evaluated in OECD 422 Reproductive and Developmental Toxicity screens. Two components of the streams in this category were assessed, 1-butene and 2-butene. Results are summarized in Tables 11 and 12.

**Table 11. Summary of Reproductive Toxicity Data for the Low 1,3-Butadiene C4 Category**

CAS RN and Chemical Name	Test Organism	OECD Test Guideline	NOAEL (ppm)
106-98-9 1-Butene	Crl:CD Rat	422	8,000 (Systemic) 8,000 (Reproductive)
107-01-7 2-Butene	Wistar Rat	422	2,500 (Systemic) 5,000 (Reproductive)
68476-52-8 C4 Crude Butadiene (10)	Crl:CD Rat	422	20,000 mg/m <sup>3</sup> (Systemic) 20,000 mg/m <sup>3</sup> (Reproductive)

**Table 12. Summary of Developmental Toxicity Data for the Low 1,3-Butadiene C4 Category**

CAS RN and Chemical Name	Test Organism	OECD Test Guideline	NOAEL (ppm)
115-11-7 Isobutylene	Wistar Rat	414	8,000 (Developmental) 8,000 (Maternal)
106-98-9 1-Butene	Crl:CD Rat	422	8,000 (Developmental) 8,000 (Maternal)
107-01-7 2-Butene	Wistar Rat	422	5,000 (Developmental) 2,500 (Maternal)
68476-52-8 C4 Crude Butadiene (10)	Crl:CD Rat	422	20,000 mg/m <sup>3</sup> (Developmental) 20,000 mg/m <sup>3</sup> (Maternal)

### Studies in Animals

#### *Effects on Fertility*

Reproductive toxicity of 1-butene ( $\geq 99\%$  purity) was evaluated in an OECD 422 Repeat Dose Reproductive/Developmental Toxicity Screen (Hoffman, 2003). Groups of 12 adult male and female Crl:CD Sprague-Dawley rats were exposed via inhalation to 1-butene at concentrations of 0; 500; 2,000; or 8,000 ppm, 6 hours/day, 7 days/week, two weeks prior to breeding, during breeding, and continuing to gestation day 19. No differences were observed in parental body weights, body weight gains, or feed consumption between the groups. No treatment related effects were observed on mating, conception, fertility, or time to mating. The NOAEL for reproductive toxicity was determined to be 8,000 ppm.

Reproductive toxicity of 2-butene (*cis* and *trans*, 95% purity) was evaluated in an OECD 422 inhalation combined repeat dose, reproductive and developmental toxicity screening test (Walkens-Brendsen and Arts, 1992). Adult male and female Wistar (Hsd/Cpd:WU) rats, 12 per sex per group, were exposed to concentrations of 0; 2,500; or 5,000 ppm 2-butene two weeks prior to breeding, during mating, and through gestation day 19. Reduced body weight change was observed in males in the first (2,500 and 5,000 ppm) and fourth week (5,000 ppm) of exposure in males. Female rats had reduced body weights during the first (5,000 ppm) and second (2,500 and 5,000 ppm) week of exposure. Reduced body weight in females was noted on lactation day 1 in the high dose group. No treatment related effects were observed on mating, conception, fertility, or time to mating. Some effects were observed in the treated and control groups. These effects included 1 stillborn pup in a high dose litter, death of one pup between postnatal days 1 and 4 in the control and low dose groups, and slightly reduced (non-significant) pup body weights in the 2,500 and 5,000 ppm groups. However, these effects were not considered treatment related. The systemic NOAEL for this study was 2,500 ppm. The reproductive NOAEL was 5,000 ppm.

Reproductive toxicity of C4 crude butadiene (CAS # 68476-52-8: 10% 1,3-butadiene; 4% isobutane; 4% n-butane; 29% *trans*-2-butene; 29% 1-butene; 11% isobutylene; and 12% *cis*-2-butene) was evaluated in an OECD 422 Repeat Dose Reproductive/Developmental Toxicity Screen (Carney *et al.*, 2001). Groups of 12 adult male and female Crl:CD Sprague-Dawley rats were exposed via inhalation to crude butadiene at concentrations of 0; 2,000; 10,000; or 20,000 mg/m<sup>3</sup>, 6 hr/day, 7 days per week two weeks prior to breeding, during breeding, continuing to gestation day 19. Male rats were exposed for 36 to 37 days. No differences were observed in parental body weights, body weight gains or feed consumption between the groups. No treatment related effects

were observed on mating, conception, fertility, or time to mating. Evaluations of gonadal function revealed no difference between treated and control groups. The NOAEL for reproductive toxicity was determined to be 20,000 mg/m<sup>3</sup>.

#### *Developmental Toxicity*

Pregnant female Wistar rats were exposed via inhalation to 0; 500; 2000; or 8000 ppm isobutylene on days 5 to 21 of gestation, 6 hr/day using the OECD 414 developmental toxicity guideline (ref). Clinical observations were performed during the exposure period. Maternal body weight, food and water consumption were frequently determined. On day 22 of gestation, dams were sacrificed and maternal and fetal evaluations were made. Exposure to isobutylene did not elicit any maternal effects. No effect was observed on number growth or survival of the fetuses in utero. Although cleft sternbrae were observed only in fetuses in the isobutylene groups, the incidence of fetuses affected was small and not dose related. Further, there were no minor changes in the appearance or ossification of the sternbrae to indicate that this area of the skeleton was adversely affected by isobutylene. In addition, there was no evidence for an adverse effect of isobutylene on other skeletal ossification centers. The maternal and developmental NOAEL was determined to be 8000 ppm.

As part of an OECD 422 Repeat Dose Reproductive/Developmental Toxicity Screen (Hoffman, 2003), no developmental toxicity was observed in Crl:CD Sprague-Dawley rats following exposure to 1-butene (≥99%). Groups of 12 adult male and female rats were exposed via inhalation to 1-butene at concentrations of 0; 500; 2,000; or 8,000 ppm, 6 hours/day, 7 days/week, 2 weeks prior to breeding, during breeding, and continuing to gestation day 19. No treatment related effects were observed in paternal body weights, body weight gains or feed consumption during the study. No difference was observed in number of viable litters, gestation length, litter size, pre implantation loss, pup body weight, or pup sex ratio. No differences were observed in pup weight gain, or in the macroscopic examination of pups. The NOAEL for this study was 8,000 ppm.

Developmental toxicity was evaluated in Wistar rats exposed to 0; 2,500; or 5,000 ppm 2-butene (*cis* and *trans*, 95% purity) during the conduct of an OECD 422 inhalation repeat dose, reproduction and developmental toxicity screen (Waalkens-Berendsen and Arts, 1992). Adult male and female Crl:CD rats were exposed to 2-butene two weeks prior to breeding, during mating, and through gestation day 19. Evaluation of developmental toxicity parameters indicated no treatment-related effects in pups. No treatment-related increase in pre-implantation loss occurred. Post-implantation loss was slightly increased in 5,000 ppm group, but was within historical control range. Total number of live births in the exposed groups was higher than controls. In the control and 2,500 ppm groups, one pup died between days 1 and 4 of lactation; viability index was 97 to 100%. Mean body weights of pups was slightly but not significantly lower in 2,500 and 5,000 ppm group, which may be explained by the higher number of pups in these groups compared to controls. No structural changes were noted in treated pups either during lactation or at necropsy. The systemic NOAEL was 2,500 ppm. The developmental NOAEL was 5,000 ppm.

As part of an OECD 422 Repeat Dose Reproductive/Developmental Toxicity Screen (Carney *et al.*, 2001), no developmental toxicity was observed in Crl:CD Sprague-Dawley rats following exposure to C4 crude butadiene (CAS # 68476-52-8: 10% 1,3-butadiene; 4% isobutane; 4% n-butane; 29% trans-2-butene; 29% 1-butene; 11% isobutylene; and 12% cis-2-butene). Groups of 12 adult male and female rats were exposed via inhalation to crude butadiene at concentrations of 2, 10, or 20 mg/L (2,000; 10,000; or 20,000 mg/m<sup>3</sup>), 6 hr/day, 7 days per week, 2 weeks prior to breeding, during breeding, and continuing to gestation day 19. No treatment related effects were observed in paternal body weights, body weight gains or feed consumption during the study. No difference was observed in number of viable litters, gestation length, litter size, pre implantation loss, pup body weight, or pup sex ratio. An increase was observed in post implantation loss in the low exposure group. This observation was considered spurious, given the lack of dose response. A single pup in

the high dose group exhibited a hernia. This finding was considered spurious due to its low incidence. The NOAEL for this study was 20,000 mg/m<sup>3</sup>.

### Conclusion

Little reproductive or developmental toxicity hazard was identified for the Low 1,3-Butadiene C4 Category. This conclusion is based on the results of OECD 422 Reproductive/Developmental Toxicity Screening studies on 1-butene and 2-butene. In these studies no reproductive or developmental toxicity was observed. Systemic effects, such as body weight changes, were observed in parental animals exposed to 2-butene. Additionally, no developmental toxicity was observed following gestational exposure to isobutylene. Further, no effect on reproductive organs was observed following subchronic exposure to isobutylene. Additional support for this conclusion can be drawn by use of rat reproductive/developmental data from the Crude Butadiene C4 Category. No adverse effects were observed in rats exposed to high levels of C4 streams. Reproductive developmental toxicity data on butane and isobutane were not available at the time this report was written. However, these data will become available as part of the API Petroleum HPV Testing Group's test plan on Petroleum gases. It is anticipated that the test results on the C4 alkanes will be similar to the results presented in this report on the C4 mono-olefins. If however, the results differ substantially this report will be re-evaluated.

## **4.2 Assessment Summary for Human Health**

Low 1,3-Butadiene C4 streams have a low order of acute toxicity. No lethality was observed at the limit concentration for 2-butene, and, other than restlessness, no toxicity was observed either. Similar results would be anticipated with other components of streams in the Low 1,3-Butadiene C4 Category. 2-Butene enantiomers were the most potent C4 olefin to induce cardiac arrest in mice after exposure to remarkably high concentrations for 20 minutes. Isobutylene and 1-butene were less potent. Thus it is reasonable to extrapolate the findings of the guideline acute toxicity study of 2-butene across the other components of the Low 1,3-Butadiene C4 Category.

There are no dermal or ocular irritation data on Low 1,3-Butadiene C4 streams or components. Therefore, read-across data for these endpoints from studies in the Crude Butadiene C4 Category were used. No dermal or ocular irritation was observed in these studies, likely due to the rapid evaporation of the test substance. As the streams in the Low 1,3-Butadiene C4 Category are gases at normal temperature and pressure, similar results would be expected.

Minimal effects were reported in repeat dose toxicity tests of several components of Low 1,3-Butadiene C4 Category streams. Reduced body weights were observed in male and female rats exposed to 2-butene resulting in a NOAEL of 2,500 ppm. A reduction in white blood cell count was observed in rats following oral exposure to 148.55 mg/kg/day isobutylene for 28 days. No adverse treatment related effects were observed in rats exposed to isobutylene for 90 days or 1-butene for 28 days via inhalation.

Test data demonstrate that Low 1,3-Butadiene C4 streams do not produce genotoxicity. No mutagenic activity was observed in *Salmonella typhimurium* reverse mutation assays in the presence or absence of metabolic activation following treatment with isobutylene, 1-butene, 2-butene, butane, or isobutane. In addition, isobutylene did not increase the number of transformed foci in mouse embryo fibroblast cells. In the mouse lymphoma assay, no evidence of mutagenic activity in mouse lymphoma L5178Y cells treated with isobutylene in culture in the presence or absence of metabolic activation. No chromosomal aberrations were observed following *in vitro* treatment with 2-butene (with and with out activation), or *in vivo* treatment with isobutylene or 1-butene. As such the Low 1,3-Butadiene C4 Category presents a low genotoxicity hazard.

Available data indicate little reproductive or developmental hazard with the streams in Low 1,3-Butadiene C4 Category. No reproductive or developmental toxicity was observed in rats exposed to

either 1-butene or 2-butene during the conduct of an OECD 422 combined repeat dose reproductive and developmental toxicity screen. No developmental toxicity was observed in a developmental toxicity study in rats exposed to isobutylene. No effect on reproductive organs was observed following repeated exposure to isobutylene in a well-conducted ninety-day subchronic toxicity study. Additionally no reproductive or developmental effects were observed in rats exposed to C4 olefin containing streams in the Crude Butadiene C4 Category.

## 5 HAZARDS TO THE ENVIRONMENT

### 5.1 Aquatic Toxicity

The aquatic toxicity of streams in this category is expected to fall within a relatively narrow range regardless of their composition. This is expected, because the constituent chemicals of these streams are neutral organic hydrocarbons whose toxic mode of action is non-polar narcosis (Ramos *et al.*, 1998). The toxic mechanism of short-term toxicity for these chemicals is disruption of biological membrane function (Van Wezel, 1995), and the differences between toxicities (i.e., LC/LL<sub>50</sub>, EC/EL<sub>50</sub>) can be explained by the differences between the target tissue-partitioning behavior of individual constituent chemicals (Verbruggen *et al.*, 2000).

The existing fish toxicity database for hydrophobic, neutral organic chemicals, which compose the streams in this category, supports a critical body residue (CBR) for these chemicals between approximately 2-8 mmol/kg fish (wet weight) (McCarty *et al.*, 1991; McCarty and Mackay, 1993). The CBR is the internal concentration of a toxicant that causes mortality. When normalized to lipid content for most organisms, the CBR is approximately 50 umol/g of lipid (Di Toro *et al.*, 2000). Therefore, only hydrocarbon streams with components of sufficient water solubility, such that their molar sum in solution is high enough to produce a total partitioning to the organism of approximately 50 umol of hydrocarbon per gram of lipid will demonstrate lethality.

Measured data are not available for the aquatic toxicity endpoints. However, structure-activity relationship (SAR) data developed with the ECOSAR model (Cash and Nabholz, 1999) were used to assess the aquatic toxicity for three trophic levels [the ECOSAR model used was from EPIWIN (1999)]. The ECOSAR model is a reliable and valid SAR model to apply to constituent chemicals from this category because it is based on a related chemical dataset that calculates the toxicity of neutral organic hydrocarbons whose toxic mode of action is non-polar narcosis. The calculated aquatic toxicity values were determined using measured log P<sub>ow</sub> values (ECOSAR requires selected physicochemical data and chemical structure to calculate effect concentrations).

Calculated aquatic toxicity values for chemicals representative of category members fall within a relatively narrow range. The effect range is a function of the range of log P<sub>ow</sub> values identified for the chemicals. Streams in this category are expected to demonstrate 96-hour LC<sub>50</sub> fish toxicity values in the range of 6.28 to 40.98 mg/L, 48-hour LC<sub>50</sub> invertebrate toxicity values in the range of 7.15 to 43.88 mg/L, and 96-hour EC<sub>50</sub> alga toxicity values in the range of 4.71 to 27.42 mg/L (Table 13).

**Table 13. Summary of Aquatic Toxicity Data for Chemical Constituents in the Low 1,3-Butadiene C4 Category**

Chemical Constituent (Log P <sub>ow</sub> *)	Fish Toxicity 96-hour LC <sub>50</sub> (mg/L)	Invertebrate Toxicity 48-hour EC <sub>50</sub> (mg/L)	Alga Toxicity 96-hour EC <sub>50</sub> (mg/L)
Isobutane (2.76)	8.32	9.39	6.13
n-Butane (2.89)	6.28	7.15	4.71
Isobutylene (2.34)	19.93	21.86	13.94
<i>cis</i> -Butene-2 (2.31)	21.26	23.28	14.81
<i>trans</i> -Butene-2 (2.33)	20.36	22.32	14.22
Butene-1 (2.40)	17.50	19.28	12.33
1,2-Butadiene (2.06**)	35.22	37.89	23.77
1,3-Butadiene (1.99)	40.98	43.88	27.42

\* The log P<sub>ow</sub> values used in the ECOSAR model are from the EPIWIN experimental database.

\*\* A measured log P<sub>ow</sub> value was not available in the EPIWIN experimental database; the calculated value was used.

## 5.2 Assessment Summary for the Environment

Results of distribution modeling show that streams in the Low 1,3-Butadiene C4 Category will partition primarily to the air compartment, with a negligible amount partitioning to water. Although constituents have a moderate degree of water solubility, wet deposition of category constituents is not likely to play a significant role in their atmospheric fate because they rapidly photodegrade. Volatilisation to the air will contribute to the rapid loss of category constituents from aqueous and terrestrial habitats. In the air, these constituents have the potential to rapidly degrade through indirect photolytic processes mediated primarily by hydroxyl radicals with calculated degradation half-lives ranging from 1.9 to 52.6 hours, depending on hydroxyl radical concentration. Aqueous photolysis and hydrolysis will not contribute to the transformation of category constituents in aquatic environments because they are either poorly or not susceptible to these reactions.

Although the biodegradability of streams in this category has not been evaluated with standard testing procedures because of their high volatility, studies have demonstrated that several category constituents can be degraded by bacteria isolated from soil and surface water samples. The results from these studies suggest that streams from this category are subject to microbial degradation. However, biodegradation is unlikely to contribute to the overall degradation of these streams because they tend to partition to the air compartment due to high volatility at ambient temperatures, and thus less likely to be available to degrading microorganisms.

Due to the fact that streams in this category are gaseous at ambient temperature and pressure and expected to partition predominantly to the atmosphere, no aquatic toxicity testing was conducted. However, the ECOSAR model was used to predict aquatic toxicity using the equation for neutral organics, a reliable estimation method for this class of chemicals. Calculated acute toxicity values of selected category constituents for fish (96-hr) and invertebrates (48-hr) range from 6.28 to 40.98 mg/L and from 7.15 to 43.88 mg/L, respectively. For algae, the calculated 96-hr EC<sub>50</sub> ranges from 4.71 to 27.42 mg/L.

**6 DATA SUMMARY**

Physico-chemical, environmental fate and effects, and human health data that characterize the seven streams in the Low 1,3-Butadiene C4 Category are summarized in Tables 14 and 15. CAS RNs are associated with streams as follows:

- **C4 Raffinate 1**
  - 68477-42-9
  - 25167-67-3
  - 68477-83-8
  - 68527-19-5
  - 68606-31-5
- **C4 Raffinate 2**
  - 68606-31-5
  - 25167-67-3
- **C4 Raffinate 3**
  - 68606-24-6
  - 25167-67-3
- **Catalytic Butylenes**
  - 25167-67-3
- **Butane**
  - 106-97-8
- **Butene-1**
  - 106-98-9
- **Isobutylene**
  - 115-11-7

**Table 14. Physico-Chemical and Environmental Data Used to Characterize Streams and CAS Registry Numbers in the Low 1,3-Butadiene C4 Category (ranges are based on data for the representative chemical subset)**

Endpoint	Low 1,3-Butadiene C4 Category Streams and CAS RNs						
	C4 Raffinate 1	C4 Raffinate 2	C4 Raffinate 3	Catalytic Butylenes	Butane	Butene-1	Isobutylene
	68477-42-9, 25167-67-3, 68477-83-8, 68527-19-5, 68606-31-5	68606-31-5, 25167-67-3	68606-24-6, 25167-67-3	25167-67-3	106-97-8	106-98-9	115-11-7
Melting Point/ Range (°C)	-145.0 to -105.5* (m)				-138.2	-145.0	-140.4
Boiling Point/ Range (°C)	-11.7 to 10.9* (m)				-0.5	-1.3	-6.9
Vapor Pressure/ Range (hPa)	1.68 E3 to 3.08 E3* (m)				2.43 E3	3.00 E3	3.08 E3
Log P <sub>ow</sub> / Range	1.99 to 2.89* (m)				2.89	2.40	2.34
Water Solubility/ Range (mg/L)	135.6 to 792.3* (m)				135.6	354.8	399.2
Direct Photodegradation	Direct photolysis will not contribute to degradation						
Indirect (OH-) Photodegradation (half-life, hrs) (a, c)	1.9 to 52.6*				48.8	4.7	2.5
Hydrolysis	Hydrolysis will not contribute to degradation						
Distribution	>99.9% partitions to air* <0.1% partitions to water*						
Biodegradation	Potential to biodegrade						
96-hr Fish Acute Toxicity (mg/L)	6.28 to 40.98* (c)				6.28	17.50	19.93
48-hr Invert Acute Toxicity (mg/L)	7.15 to 43.88* (c)				7.15	19.28	21.86
96-hr Alga Toxicity (mg/L)	4.71 to 27.42* (c)				4.71	12.33	13.94

\* Constituent chemicals used to define selected endpoints include: isobutane; n-butane; isobutylene; cis-butene-2; trans-butene-2; butene-1; 1,2-butadiene; 1,3-butadiene  
(m) Measured values (a) Atmospheric half-life values are based on a 12-hr day. (c) Calculated values

**Table 15. Human Health Data Used to Characterize Streams and CAS Registry Numbers in the Low 1,3-Butadiene C4 Category**

Endpoint	Human Health Data for Low 1,3-Butadiene C4 Category Streams (CAS RNs)								
	C4 Raffinate 1	C4 Raffinate 2	C4 Raffinate 3	Catalytic Butylenes	Butane	Butene-1	Isobutylene	Butene-2*	Isobutane*
	68477-42-9, 25167-67-3, 68477-83-8, 68527-19-5, 68606-31-5	68606-31-5, 25167-67-3	68606-24-6, 25167-67-3	25167-67-3	106-97-8	106-98-9	115-11-7	107-10-7	75-28-5
Acute Toxicity (rat)	>10,000 ppm								
Irritation	Non irritating (eyes / skin)								
Repeat Dose Toxicity	>2,500 ppm								
Mutagenicity Ames Assay	Negative								
Mutagenicity Mouse Micronucleus	Negative								
Reproductive Toxicity (rat)	>5,000 ppm (fertility) >2,500 ppm (parental)								
Developmental Toxicity (rat)	>5,000 ppm (fertility) >2,500 ppm (parental)								

\* Not a member of the category, but data are include because these substances represent major components of the mixed streams within the category.

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**APPENDIX I****ETHYLENE PROCESS DESCRIPTION****A. Ethylene Process****1. Steam Cracking**

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 unsaturates. 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 streams. 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 streams are also formed, including other olefins, diolefins, aromatics, paraffins, and lesser amounts of acetylenes. These other hydrocarbon streams include compounds with two or more carbon (C) atoms per molecule, i.e., C2, C3, C4, etc. Propane and propylene are examples of C3 hydrocarbons and benzene, hexene, and cyclohexane are examples of C6 hydrocarbons.

**2. Refinery Gas Separation**

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 primarily 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 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 pressurized systems.

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. Further

processing of one of these mixed streams, the Crude Butadiene C4 stream, results in additional mixed streams and high purity products that make up the main constituents of the Low 1,3-Butadiene C4 Category. Categories sponsored by the Olefins Panel of the American Chemistry Council are listed in Table 16.

**Table 16. HPV Program Categories Sponsored by the Olefins Panel of the American Chemistry Council**

<b>Category Number</b>	<b>Category Name</b>
1	Crude Butadiene C4
2	Low 1,3-Butadiene C4
3	C5 Non-Cyclics
4	Propylene Streams
5	High Benzene Naphthas
6	Low Benzene Naphthas
7,8,9	Resin Oils & Cyclodiene Dimer Concentrates
10	Fuel Oils
11	Pyrolysis C3+ and Pyrolysis C4+

The chemical process operations that are associated with the process streams in the Low 1,3-Butadiene C4 Category are shown in Figure 4.

**Figure 4. Low 1,3-Butadiene C4 Process Streams Flow Diagram from the Ethylene Manufacturing Process Unit**

