

## Category H 'high benzene naphthas' - Chemical Category Justification

(NB : all compositions are in w/w for liquids and v/v for gases)

<b>Category definition and its members</b>	
<b>1.1.</b>	<b>Category Definition</b>
<b>1.1.a.</b>	<b>Category Hypothesis</b>
<p>The <b>high benzene naphthas</b> category is driven by benzene as Category 1 Carcinogen, Category 2 Mutagen. All streams containing 0.1% or more benzene to be considered for inclusion. This category contains hydrocarbons (aliphatic, aromatic and olefinic) with carbon numbers predominantly in the C5-C12 range and boiling from 30C to 300C. Members of this category contain &gt;0.1% benzene and contain varying amounts of toluene, xylenes and n-hexane. Some category members contain PAHs, where this is the case anthracene has been quantified. Some category members contain 1,3-butadiene and this has been quantified where needed. Category members are usually produced by the distillation of products from a steam cracking process or by pyrolysis Companies importing streams will need to confirm that such streams meet the chemical description and are in domain. The category contains streams that have claimed compositions of single substances up to over 80%. These are not considered as pure substances as the variability during manufacture is such that this is not always the case and usually the production processes are not designed to make substances at such a high purity.</p> <p>By definition, from the category, these streams have overlapping hydrocarbon compositions, within a defined range, and hence, will have similar properties. It is therefore reasonable to assume that the components of the high benzene naphthas will behave in a reasonably predictable manner, and with respect to phys-chem and environmental fate and effect properties read-across is valid.</p> <p>For mammalian endpoints, the category members are liquids that are of moderate to low volatility. Inhalation and skin contact represent the primary route of exposure. Benzene, as a component at greater than 0.1% in all streams in this category is considered the key driver in establishing and assessing health effects. It can therefore be assumed that streams meeting the applicability domain will behave in a similar manner and that the use of read-across is valid.</p> <p>For mammalian endpoints, the classification of these streams will be driven by the content of benzene as this is more than 0.1% w/w for all category members.</p>	
<b>1.1.b.</b>	<b>Applicability domain (AD) of the category</b>
<p>The category applies to streams with the following PIONA* analysis: predominantly (Iso)Paraffins, olefins, naphthenics and aromatics and more than 0.1% benzene and a carbon number range of predominantly 5-12.</p> <p><i>Boiling Point – the streams in this category will boil predominantly in the range of 30 - 300°C</i></p> <p><b>Specific components</b> (The range entered below is that currently based on received analytical data, it is not intended to be prescriptive. See section 1.3).</p> <p><i>Benzene: 0.1 – 90%</i></p> <p><i>Toluene: 0.1 – 98%</i></p> <p><i>Hexane: up to 20%</i></p> <p><i>Xylenes: up to 75%</i></p> <p><i>1,3-butadiene: &lt;0.1% to 1%</i></p> <p><i>Naphthalene: up to 30%</i></p> <p><i>Isoprene: up to 6%</i></p> <p><i>Anthracene : up to 1% (streams with this component at &gt;0.1% are candidates for authorisation as anthracene is a confirmed PBT)</i></p>	

**PIONA\* :**

(iso)Paraffins – up to 90% : C# 5 - 12

Olefins – up to 35% : C# 5 - 12

Naphthenics – up to 80% : C# 5 - 12

Aromatics – up to 100% : C# 5 – 12

\*: PIONA refers to a description of the type of hydrocarbons present, paraffins, isoparaffins, olefins, naphthenics and aromatics. It does not refer to a specific type of analysis or determination.

**1.2. Category Members**

CAS Number	CAS Description	Registered Substance Name
102110-55-4	Residues (petroleum), steam-cracked light, arom.	Residues (petroleum), steam-cracked light, arom.
64741-47-5	Natural gas condensates (petroleum)	Natural gas condensates (petroleum) (condensate)
		Natural gas condensates (petroleum)
64741-84-0	Naphtha (petroleum), solvent-refined light	Naphtha (petroleum), solvent-refined light
64741-99-7	Extracts (petroleum), light naphtha solvent	Extracts (petroleum), light naphtha solvent
64742-83-2	Naphtha (petroleum), light steam-cracked	Naphtha (petroleum), light steam-cracked; Low boiling point naphtha – unspecified
		Pyrolysis gasoline
		SCN heartcut
		Naphtha (petroleum), light steam-cracked
	Naphtha (petroleum) light steam-cracked. (Aromatics mixture-Pyrolysis Gasoline)	
64742-91-2	Distillates (petroleum), steam-cracked	Distillates (petroleum), steam-cracked
68410-96-8	Distillates (petroleum), hydrotreated middle, intermediate boiling	Distillates (petroleum), hydrotreated middle, intermediate boiling
68475-70-7	Aromatic hydrocarbons, C6-8, naphtha-raffinate pyrolyzate-derived	Aromatic hydrocarbons, C6-8, naphtha-raffinate pyrolyzate-derived
68477-39-4	Distillates (petroleum), cracked stripped steam-cracked petroleum distillates, C8-10 fraction	Distillates (petroleum), cracked stripped steam-cracked petroleum distillates, C8-10 fraction
68477-53-2	Distillates (petroleum), steam-cracked, C5-12 fraction	distillates(petroleum), steam cracked, C 5-12 fraction
68513-69-9	Residues (petroleum), steam-cracked light	SC Polymers
		Residues (petroleum), steam-cracked light
68516-20-1	Naphtha (petroleum), steam-cracked middle arom.	Naphtha (petroleum), steam-cracked middle arom.
		Xylene rich
		Naphtha (petroleum) steam-cracked

		middle arom. (Aromatic concentrate)
68527-23-1	Naphtha (petroleum), light steam-cracked arom.	Naphtha (petroleum), light steam-cracked arom.
		C7+ Gasoline component (PYGAS TAIL C8+)
68527-26-4	Naphtha (petroleum), light steam-cracked, debenzenized	Naphtha (petroleum), light steam-cracked, debenzenized. Low boiling point naphtha - unspecified.
		Aromatic stream (C8-C10)
		Naphtha (petroleum), light steam-cracked, debenzenized
68606-10-0	Gasoline, pyrolysis, debutanizer bottoms	Gasoline, pyrolysis, debutanizer bottoms
		Pygas (chemcracker)
68921-67-5	Hydrocarbons, ethylene-manuf.-by-product distn. residues	Hydrocarbons, ethylene-manuf.-by-product distn. residues
		Pyrolysis Gasoline
68955-29-3	Distillates (petroleum), light thermal cracked, debutanized arom.	Distillates (petroleum), light thermal cracked, debutanized arom
90641-13-7	Naphtha (petroleum), steam-cracked, hydrotreated, C9-10-arom.-rich	Naphtha (petroleum), steam-cracked, hydrotreated, C9-10-arom.-rich.
90989-41-6	Aromatic hydrocarbons, C6-10, C8-rich	Aromatic hydrocarbons, C6-10, C8-rich
90989-43-8	Aromatic hydrocarbons, C7-8, ethylene-manuf.-by-product	Aromatic hydrocarbons, C7-8, ethylene-manuf.-by-product
91723-50-1	Hydrocarbons, C5-7, C6-rich, ethylene manuf. by-products	Hydrocarbons, C5-7, C6-rich, ethylene manuf. by-products
91995-50-5	Distillates (petroleum), naphtha steam cracking-derived, hydrotreated light arom.	Distillates (petroleum), naphtha steam cracking-derived, hydrotreated light arom.
92045-57-3	Naphtha (petroleum), hydrotreated light steam-cracked	Naphtha (petroleum), hydrotreated light steam-cracked
		Naphtha (petroleum), hydrotreated light steam-cracked; Low boiling point hydrogen treated naphtha
92045-61-9	Hydrocarbons, C4-12, naphtha-cracking, hydrotreated	Hydrocarbons, C4-12, naphtha-cracking, hydrotreated
94114-03-1	Gasoline, pyrolysis, hydrogenated	Gasoline, pyrolysis, hydrogenated.
		Gasoline, pyrolysis, hydrogenated; Low boiling point naphtha-unspecified
98219-47-7	Naphtha (petroleum), light steam-cracked, thermally treated	Naphtha (petroleum), light steam-cracked, thermally treated.
		Naphtha (petroleum), light steam-cracked, thermally treated; Low boiling point naphtha - unspecified
		Naphtha (petroleum), light steam-cracked, thermally treated (pygas)

**1.3. Purity / Impurities**

The substances in this category are UVCBs and as such are considered to be 100% pure. The term impurity is not relevant for UVCBs, however, substances will be described using the following:

- Known constituents present at 10% or greater (if any), identified by IUPAC name and EC number/CAS number, indicating typical concentrations and/or concentration ranges;
- Constituents relevant for hazard classification (if any);

- Constituents relevant for PBT assessment (if any).

### Primary marker

Benzene (CAS# 71-43-2): tox classification: T, Carc Cat 1 R45, Mut Cat 2 R46, R36/38, R48/23/24/25, R65

### Tox statements:

Benzene is regulated as a non-threshold carcinogen shown to cause heritable genetic damage in germ cells in experimental animals and toxicity to blood forming elements present in bone marrow. It is irritating to eyes and skin and presents an aspiration hazard.

### 2. Category justification

The **high benzene naphthas** category is driven by benzene as Category 1 Carcinogen, Category 2 Mutagen. This category contains hydrocarbons (aliphatic, aromatic and olefinic) with carbon numbers predominantly in the C5-C12 range and boiling from 30 °C to 300 °C. Members of this category contain >0.1% benzene and contain varying amounts of toluene, xylenes and n-hexane. In addition some category members contain PAHs and 1,3-butadiene and this has been quantified where possible. The physico-chemical properties associated with these types of UVCBs indicated that they comprise a category based on the range of boiling points (from 45°C to 340°C) and will have similar behaviour in the environment. The log Kow ranges from 2.2 to >6.5 and the streams in this category are not considered to be readily biodegradable. The mammalian toxicity information and environmental assessment also indicated that the streams in this category exert similar effects.

### 3. Data matrix

**High benzene naphthas** is a UCVB category and therefore identification of trends between category members is not appropriate and therefore, according to the ECHA Guidance on information requirements and chemical assessment Chapter R.6, it is not feasible to establish a full data matrix for this category. Consequently, a data set that applies to all members of this category has been developed.

### 4. Conclusions per endpoint for C&L, PBT/vPvB and dose descriptor

#### CLASSIFICATION AND LABELLING

#### Physico-chemical Hazard Assessment

- **Boiling point** - The boiling point of streams in this category was ranged from 45°C to 340°C
- **Partition coefficient** - The streams in this category have partition coefficients ranges from log Kow 2.2 to >6.5.
- **Flash point** - The flash point of streams in this category is -20.5 °C to 35 °C.

Flashpoint of < 23 °C and initial boiling point ≥ 35 °C.

Flam. Liquid 2 (Hazard statement: H225: Highly flammable liquid and vapour.

Flashpoint of ≥ 23 °C and initial boiling point ≤ 60 °C.

Flam. Liquid 3 (Hazard statement: H226: Flammable liquid and vapour.

#### Human Health Hazard Assessment

- **Toxicokinetics** – The marker substances, in their pure form, have well-defined toxicokinetic

parameters that have been taken into account during the derivation of their respective DNEL's. The overall DNEL of this category is driven by the DN(M)EL for benzene.

- **Acute toxicity** – High Benzene Naphtha streams are of low acute toxicity by the dermal and inhalation routes and do not warrant classification for these end-points. High Benzene Naphtha streams are considered to present an aspiration hazard following oral exposure and those that  $\geq 25\%$  naphthalene are considered to be acutely toxic. Streams that contain a total concentration of  $\geq 20\%$  toluene and n-hexane are likely to cause drowsiness.
- **Irritation** – High Benzene Naphtha streams should be considered to be skin and eye irritants and to be classified appropriately. The need for classification with respect to respiratory tract irritation is dependent upon available data for the specific stream or the concentration of xylenes in the stream.
- **Sensitisation** – Not skin or respiratory sensitisers.
- **Repeat dose toxicity** – The limited repeat dose toxicity data on specific streams identified for this category (dermal toxicity studies for API 83-04 [light catalytic reformed naphtha] and API 83-05 [catalytic reformed naphtha]) provided no evidence of systemic target organ toxicity. However, there are substantial data on the repeated dose toxicity of a number of specific components present in some streams i.e. benzene, toluene and hexane which demonstrate significant target organ toxicity and when present at concentrations greater than or equal to 1%, 10% or 10% respectively will drive the mammalian toxicity effects.
- **Genetic toxicity** – *In vitro* and/or *in vivo* genotoxicity data are available for 1 stream within this category (CAS 64742-83-2 [C4 crude butadiene]) and 2 related streams (API 83-04 [light catalytic reformed naphtha] and API 83-05 [catalytic reformed naphtha]). These studies show both positive and negative results. As benzene is a Category 2 mutagen and is present in all streams at a concentration of 0.1% or greater then High Benzene Naphtha streams are considered to be mutagenic.
- **Carcinogenicity** – There are no specific carcinogenicity data on any of the streams within this category. However, there are substantial data on the carcinogenicity of a number of specific components present in some streams. Of these, benzene, 1,3-butadiene, naphthalene and isoprene have been shown to be carcinogenic. High Benzene Naphtha streams are considered to be carcinogens as they contain  $\geq 0.1\%$  benzene and may contain up to 1% 1,3-butadiene, up to 30% naphthalene and up to 6% isoprene.
- **Toxic to reproduction** – It is recognised that there are data gaps for both developmental toxicity study and multi-generation studies. These studies do not need to be conducted as High Benzene Naphtha streams contain at least 0.1% benzene which is known to be mutagenic and carcinogenic. Available data on marker substances are sufficient for classification and labelling purposes. For streams that contain n-hexane at concentrations greater than or equal to 5% (EU/DPD) or 3% (GHS/CLP), classification is required for effects on fertility. For streams that contain toluene at concentrations greater than or equal to 5% (EU/DPD) or 3% (GHS/CLP), classification is required for developmental toxicity.

#### Environmental Hazard Assessment

- **Biodegradation** - Based on two experimental studies the streams in this category have not been shown to be readily biodegradable and will not be considered readily biodegradable.
- **Bioaccumulation** - The calculated log BCF for representative components of the streams in

this category are in the range 0.73-4.15.

- **Ecotoxicity** – There were three short term ecotoxicity studies available for each of the three trophic levels for category members. All studies indicate an LL50 of 1.1 mg/l to 4.4 mg/l.

Based on the available experimental data (96 hr LL50 1.1mg/l WAF) streams in this category should have the classification R51/53 under the DSD and Aquatic Chronic 2 under the CLP regulations.

### **CONCLUSION FOR PBT**

The screening assessment of the available data indicates that the properties of the members of this category do not meet the specific criteria detailed in Annex XIII or do not allow a direct comparison with all the criteria in Annex XIII but nevertheless indicate that the substance would not have these properties and therefore are not considered PBT/vPvB.

### **CONCLUSION FOR DOSE DESCRIPTOR**

**Environment:** Deriving PNECs for UVCB substances based on WAF information is inappropriate. As the substance is a hydrocarbon UVCB the hydrocarbon block method has been used for environmental risk assessment (see REACH guidance, R7, app.13-1). The Petrorisk model (Redman, A. (2010). PETRORISK Users Guide, HydroQual, Inc., for Conservation of Clean Air and Water in Europe (CONCAWE)), was used for the environmental assessment. Blocks of C5-C12 carbon atoms and with a boiling point range of 34.5°C to 307.9 °C were used in the modelling exercise. The model assigns individual structures from the library to the hydrocarbon blocks that the user enters. The input parameters are provided in Appendix B of the CSR. Details of the library structure mapping, some relevant physico-chemical properties and the mass fraction that is assigned to each chemical are also found in this appendix.

#### **Human Health:**

These hydrocarbon streams are used as intermediates, in manufacture and as fuels. Benzene is present at  $\geq 0.1\%$  by weight hence with the exception of motor fuels (which are the subject of a separate directive, 98/70/EC) supply of these streams to the general population is not permissible.

The DNELs address concerns linked to the CMR properties of the marker substances or their potential to cause other long-term health effects leading to an equivalent level of concern. Risk characterization will be based on the premise that a marker substance with a low DN(M)EL present at high concentration in a stream will possess a greater relative hazard potential than a marker substance with a higher DN(M)EL present at the same or lower concentration. It will also focus on the potential of the markers to cause serious long-term health effects rather than on short-term or irritation-related changes.

Against that background, the most hazardous marker substances present in these streams are highlighted in the following table:

Marker substance	Indicative concentration (%)	Inhalation		Dermal	
		DN(M)EL mg/m <sup>3</sup>	Relative hazard potential (max % ÷ DN(M)EL)	DN(M)EL mg/kg bw/d	Relative hazard potential (max % ÷ DN(M)EL)
benzene	0.1 to 90	3.25	27.7	23.4	3.85
toluene	0.1 to 98	192	0.51	384	0.26
hexane	Up to 20	72	0.27	25.9	0.772
xylenes	Up to 25	221	0.11	3182	0.008
1,3-	<0.1 to 1	2.21	0.45	na <sup>1</sup>	na

butadiene					
naphthalene	Up to 30	50	0.6	72	0.42
isoprene	Up to 6	8.4	0.71	23.7	0.25
anthracene	Up to 1	<i>low systemic toxicity, no DNELs required</i>			
<sup>†</sup> - 1,3-Butadiene is a gas at room temperature and therefore exposure by the dermal route is not relevant.					

Hence demonstration of “safe use” for worker inhalation and dermal hazards associated with the presence of benzene will also provide adequate protection against hazards arising from other marker substances present. The long term inhalation and long term dermal DNELs for benzene will therefore be used for workers.