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GDCh-Advisory Committee
on Existing Chemicals of
Environmental Relevance (BUA)

Liquefied petroleum gas (LPG)

(Propane, Butane, Isobutane
and Mixtures)

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on Existing Chemicals of Environmental Relevance (BUA)

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Beratergremium für
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Foreword

The German Chemicals Act (Chemikaliengesetz - ChemG) of 1980 stipulates that certain existing chemicals must be reported to the competent authority, if they exhibit properties which indicate that they may be hazardous, either alone or in combination with other substances.
In the summer of 1982, an Advisory Committee on Existing Chemicals of Environmental Relevance (BUA) was set up by the German Chemical Society (Gesellschaft Deutscher Chemiker - GDCh). It brings together representatives from the scientific community, the chemical industry and the governmental authorities. This Advisory Committee is responsible for elaborating appropriate solutions for substances of relevance for health and the environment on the basis of voluntary measures. It selects and examines existing chemicals from the aforementioned angles. The testing and evaluation are based on scientific criteria alone.
It was, therefore, necessary to develop priority setting procedures. In a first phase reports were only prepared for priority chemicals. Within the framework of a first priority setting procedure, chemicals were compiled from several priority lists and 135 chemicals were selected for detailed substance reports.
In a second priority setting procedure the survey of the German Chemical Industry Association (VCI) on all substances with a production volume of more than 10 tons per year was used as a starting list. Since this survey covered 4,600 chemicals, BUA decided to process the corresponding list in several stages. The first stage included approx. 1,050 substances with a production volume of more than 1,000 tons per year.
Detailed reports are drawn up on chemicals suspected of having a hazard potential and abridged reports on those presenting only a minor hazard potential, according to the current state of knowledge.
The detailed BUA reports take in both the published literature and data from industry. If data for the evaluation of the chemicals are not available, additional studies are recommended and the results are published as updates to the reports. The reports serve as a basis for the instigation of administrative measures, when there are indications of risks to health or the environment.

Tübingen, May 1993

Ernst Bayer
Chairman of the Advisory Committee
on Existing Chemicals
of Environmental Relevance

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BUA Report on Liquefied petroleum gas

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Liquefied Petroleum Gas (LPG) is a natural constituent of crude oil and natural gas. LPGs obtained in crude oil or natural gas production are reblended into the stabilized crude oil and sent to the mineral-oil refineries. Propane and butane are separated in special distillation towers, the gas recovery units. They are marketed as LPG by the petroleum industry either directly as propane and butane or as mixtures of the two.

According to the published mineral-oil data the LPG production of the refineries amounted to

1991 2 358 000 t
1992 2 583 000 t

The average LPG production for the years 1987-1992 can be calculated to 2.7 % (m/m) on crude.

LPG consists mainly of propane, isobutane and butane. It may also contain other hydrocarbons, in concentrations above 1 % (mm) ethane, propene, butenes and isopentane. In Germany the butadiene content of LPG usually is below 0.1 % (m/m). The German LPG standards require a minimum level of 95 % (m/m) of C_3- or C_4-hydrocarbons respectively. The composition of commercially used LPGs may vary within these limits to a considerable amount.

This BUA report mainly refers to the main LPG constituents propane, isobutane und butane. Ethane, propene, butenes and isopentane will not be covered in detail.

1991 appr. 4.1 million t of LPG were used in Germany:

- In the refineries appr. 30 % were blended into gasolines. This portion is statistically classified as gasoline, for example in “Amtliche Mineralöldaten für die Bundesrepublik Deutschland (Official Mineraloil-Data of the Federal Republic of Germany) and “MWV Mineralöl-Zahlen (MWV Mineraloil-Data)”.
- Its main use was as a fuel for heating and illumination purposes (appr. 47 %), a minor amount (appr. 1.5 %) was used for motor operations. Due to their small amounts the use as automotive gas (appr. 3 000 t) and as aerosol propellent (appr. 22 250 t) are statistically not listed separately, but are included in the aforementioned figures.
- Due to existing economic incentives an essential portion (appr. 21 %) was used as feed stock for steamcracking Operations.

The natural emissions of LPG into the atmosphere and hydrosphere cannot be quantified. The physico-chemical properties (vapor pressure, Henry‘s constant, chemical structure) indicate that all LPG emitted into the various compartments will almost completely enter the atmosphere after short periods of time.

Based on the available data the total release into the atmosphere can roughly be estimated to appr. 215 240 t/a for the year 1991. This figure does not include any emissions from combustion processes. The combustion of gasolines in car engines will additionally provide emissions of appr. 42 000 t/a of saturated and unsaturated C_3- and C_4-hydrocarbons in the Federal Republic of Germany.

In ocean water average concentrations of C_2-C_4-hydrocarbons were determined in the ng/l range. Data are not available for the rivers of the Federal Republic of Germany.

In the Federal Republic of Germany maximal concentrations of 22.6 µg/m^3 of propane, 26.6 µg/m^3 of isobutane and 55.7 µg/m^3 of butane were found in air samples.

During 1984/1985 a very extensive study investigated workplaces involved in the manufacture and distribution of gasoline. On the basis of 540 personal gasoline exposure measurements in 13 European countries the C_3-C_4-concentrations in gasoline vapor amounted to appr. 37 % (m/m). 8 hour time-weighted average exposures of 1.6 mg/m^3 of propane, 12.1 mg/m^3 of isobutane and 26.6 mg/m^3 of butane were determined as average figures in long-term personal samples at 12 workplaces (318 measurements). At self-service stations customers were exposed to maximal concentrations of 8.2 mg/m^3 of propane, 34.4 mg/m^3 of isobutane and 74.0 mg/m^3 of butane (2 min time-weighted average) as average of 21 measurements.

Degradabllity

Bacteria capable of growth on hydrocarbons which are available in LPG suggest the possible degradation of these hydrocarbons.

The hydrolytic degradation of the simple alkanes/alkenes is not possible due to their chemical structure.

Calculation of the reactivities towards OH radicals result in atmospheric half-lives between 0.3 and 13.3 days.

Bioaccumulation, geoaccumulation

According to the available values for the log P_{OW} from 1.74 to 2.89 - only isopentane with an average content of 1.2 % (m/m) in butane has a log P_{OW} of 3.21 - appreciable bioaccumulation seems unlikely. In addition the physico-chemical data do not indicate any geoaccumulation.

Ecotoxic effects

There are no studies available regarding the effects of LPG on aquatic organisms.

Mycobacterium vaccae and *Mycobacterium phlei* were capable of growth on propane, isobutane and butane. The lysis of whole cells and cell-wall fragments of *Micrococcus lysodeikticus* by egg-white lysozyme was inhibited by the same hydrocarbons. The inhibitory action of hydrocarbons present in LPG on the enzymatic catabolism of bacterial spores was demonstrated.

According to the available study results alkanes have only minor effects on plants. The series of alkenes contains differently effective hydrocarbons from the phytotoxic ethene over the still active propene and 1-butene to the inert 2-butenes.

Toxicological aspects

There are no special reports of toxicity studies on LPGs. However, information published on the major components propane, isobutane and butane is useful for predicting the possible toxicity of LPG.

The hydrocarbons are primarily resorbed by the respiratory tract and partly exhaled unchanged via the lungs.

Secondary and tertiary alcohols are obtained by the microsomal hydroxylation of the lower members of the alkanes. The secondary alcohols are oxidized to ketones by the dehydrogenase system, while the tertiary alcohols are rather stable and will only be metabolized to a small extent.

In mammals propane, isobutane and butane are considered as slightly toxic after acute inhalative application. The LC_{50} for the rat has been reported as 658 mg/l/4 h for butane, 1379 mg/l/15 min for isobutane and > 1465 mg/l/15 min for propane. Acute intoxication is manifested in CNS depression. Butane demonstrated greater narcotic and lethal effects than isobutane. After inhalation cardiac sensitization to adrenalin in dogs has been reported.

Studies on genotoxicity of propane and butane did not show any mutagenic activity in bacterial systems with Salmonella typhimurium (TA 98, TA 100, TA 1535, TA 1537, TA 1538) with and without metabolic activation.

LPG vapor is not a respiratory irritant for man. Increasing concentration and exposure time will result in narcotic effects. High concentrations may result in loss of consciousness, convulsions and even asphyxiation as a consequence of oxygen deficiency. The narcotic effect of butanes is greater than with propane.

Operating experiences have shown that propane, isobutane and butane are non-irritating and without a sensitizing effect. In direct contact to the skin erythema and oedema formation as well as necrosis by cold burns were observed.

Longtime exposed workers at a LPG filling station reported symptoms such as throat dryness, dry cough, excitability and sometimes giddiness. Medical investigation revealed harsh respiration, dyspnoea, tachycardia, sometimes joined with extrasystolic arrhythmia and pain to epigastrium palpation.

There are no data available on repeated application, clastogenicity, cancerogenicity and reproduction toxicity.

Recommendations

Ecotoxicity

The available studies on the ecotoxic effects and the behaviour in the environment are considered adequate for the evaluation of the three main LPG-constituents propane, isobutane and butane.

Toxicity

The three main constituents propane, isobutane and butane are inert gases which lead to intoxications only at very high concentrations, particularly in case of oxygen deficiency in the breathing air. Specific toxic effects will not be expected so that the missing investigations on repeated application, clastogenicity, cancerogenicity and reproduction toxicity are not required.

In so far as the LPG contains other hydrocarbons in relevant quantities these must be considered in the toxicological evaluation.

Carrying out further toxicological studies with LPG samples is not regarded as useful because the composition varies and further relevant evidence cannot be expected.