

Utsläpp av butan på ett oljeraffinaderi.

860515 MARS 1986_14

En läcka uppstod under rutinmässig drift på ett oljeraffinaderi. Läckan hade uppstått till följd av korrosion i en rörkrök. Automatiska sensorer kände av läckan och gav larm samtidigt som läckan observerades av en förbipasserande arbetare. Läckan bekräftades och skiftpersonalen gjorde bedömningen att ett utsläpp av LPG inte gick att undvika. LPG i detta fall var isobutan. Efter att ha aktiverat nödgärder som isolering och tryckreducering tillkallade man företagets interna brandkår och räddningstjänsten. Räddningstjänsten anlände mycket snabbt och till följd av en god förtrogenhet med raffinaderiområdet hade man monterat 20 stycken vattenkanoner på mycket kort tid. Man upprätthöll vattenbesprutningen under den tid som det tog att sänka tryck på rörledningarna så mycket att reparationsarbetet kunde påbörjas. Det kritiska stadiet varade i en timme. En måttlig vind förde gasen bort från anläggningen. Gashalterna föll mycket snabbt under nivåer där risk för antändning förekommer.

Inblandade ämnen och mängder

	CAS Nr.	Mängd
isobutan	106-97-8	4400 kg
vätefluorid (förorening i butangasen)	7664-39-3	4,4-8,8 kg

Skador:

Människor: Inga.

Materiella:

Miljö/ekologi: Inga effekter rapporterade.

Infrastruktur:

Erfarenheter redovisade (Ja/Nej):

Kortfattat anges förebyggande åtgärder.

Report Profile

Identification of Report:

country: FA ident key: 1986_014_01

reported under Seveso I directive as major accident reports: SHORT+FULL

Date of Major Occurrence: Time of Major Occurrence

start: 1986-05-15 start: 09:00:00

finish: finish:

Establishment:

name:

address:

industry: 2002 petrochemical, refining, processing

Oil Refinery

Seveso II status: not applicable: Yes art. 6 (notification): No

art. 7 (MAPP): No

art. 9 (safety report): No

Date of Report:

short: full:

Authority Reporting:

name:

address:

Authority Contact:

rep_cont_name:

rep_cont_phone:

rep_cont_fax:

Additional Comments:

a) - not applicable -

b) - not applicable -

c) - not applicable -

d) - not applicable -

e) - not applicable -

Short Report

country: FA **ident key:** 1986_014_01

Accident Types:

release: Yes **explosion:** No

water contamination: No **other:** No

fire: No

description:

ENVIRONMENT AND ATMOSPHERICAL CONDITIONS:... see Appendix Short Report / description of accident types

Substance(s) Directly Involved:

toxic: Yes **explosive:** Yes

ecotoxic: No **other:** No

flammable: Yes

description:

- Isobutane (C.A.S. CODE: 106-97-8): amount involved = 4,400 kg... see Appendix Short Report / description of substances involved

Immediate Sources of Accident:

storage: No **transfer:** No

process: Yes **other:** No

description:

A leak occurred in an 8" bore steel pipe which formed one leg of an isobutane recycle stream. Flow through the pipe at the time of the leak was approximately 60,000 kg/h at a temperature of 84°C and a pressure of 15 barg.

The isobutane conta... see Appendix Short Report / description of immediate sources

Suspected Causes:

plant or equipment: Yes **environmental:** No

human: No **other:** No

description:

INITIATING EVENT AND CONSEQUENCES:... see Appendix Short Report / description of suspected causes

Immediate Effects:

material loss: No

human deaths: No

human injuries: No **community disruption:** No

other: Yes

ecological harm: No

national heritage loss: No

description:

OTHER:

No material losses occurred except released isobutane and hydrogen fluoride.

Emergency Measures taken:

on-site systems: Yes **decontamination:** No

external services: Yes **restoration:** No

sheltering: No **other:** No

evacuation: No

description:

INTERNAL TO THE ESTABLISHMENT:... see Appendix Short Report / description of emergency measures taken

Immediate Lessons Learned:

prevention: Yes **other:** No

mitigation: Yes

description:

MEASURES TO PREVENT ANY RECURRENCE OF SIMILAR ACCIDENTS:... see Appendix Short Report / description of immediate lessons learned

A Occurrence Full Report

country: FA **ident key:** 1986_014_01

1 Type of Accident

remarks: Owing to corrosion in an isobutane recycle piping system, a leak of isobutane containing traces of hydrogen fluoride occurred (code 1101). The gas cloud dispersed safely without igniting (it was diluted below the low flammable limit within ... see Appendix Full Report A / type of accident

2 Dangerous Substances

remarks: The total establishment and the potential directly involved inventories of isobutane and hydrogen fluoride refer to the amounts released during the accident. The concentration of hydrogen fluoride in the isobutane stream varied between 0.1% ... see Appendix Full Report A / dangerous substances

3 Source of Accident

illustration: - not applicable -

remarks: The leak occurred in a 8" bore steel pipe (code 4011) which was one leg of an isobutane recycle stream. The recycle stream section (operating at 84°C, 15 barg) was a part of the Alkylation unit of a conventional oil refinery (code 2002). In... see Appendix Full Report A / source of accident - remarks

4 Meteorological Conditions

precipitation none: fog: rain: hail: snow:

No No No No No

wind speed (m/s):

direction (from):

stability (Pasquill):

ambient temperature (°C):

remarks: A moderate breeze blew the released gas away from the plant and nearby installations.

5 Causes of Major Occurrence

main causes

technical / physical 5102 operation: component/machinery failure/malfunction

5104 operation: corrosion/fatigue

- not applicable -

- not applicable -

- not applicable -

human / organizational 5307 organization: process analysis (inadequate, incorrect)

- not applicable -

- not applicable -

- not applicable -

- not applicable -

remarks: The failure of the isobutane recycle piping (code 5102) was due to an internal corrosion.

Examination of the pipe revealed that a plug of rust and sludge containing 9.9% FeF2, 8.1%

FeF3 and 37.5% Fe2O3 had accumulated at the base of a shall... see Appendix Full Report A

/ causes of major occurrence

6 Discussion about the Occurrence

- not applicable -

Type of Accident country: FA ident key: 1986_014_01

event:

major occurrence 1101 release: gas/vapour/mist/etc release to air

initiating event 1101 release: gas/vapour/mist/etc release to air

associated event - not applicable -

Dangerous substances

country: FA ident key: 1986_014_01

a) total establishment inventory

CAS number: 106-97-8 **identity:** Isobutane

name from Seveso I Directive: - not applicable -

name from Seveso II Directive: - not applicable -

category from Seveso II: - not applicable -

other hazards (1): - not applicable -

other hazards (2): - not applicable -

maximum quantity (tonnes): 4,4

use of substance as: NORMAL FINISHED PRODUCT

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: 4,4 **potential quantity:** 4,4

c) substance belongs to relevant inventory indirectly involved: No

actual quantity: -1 **indir_pot_quant:** -1

a) total establishment inventory

CAS number: 7664-39-3 **identity:** Hydrogen Fluoride

name from Seveso I Directive: - not applicable -

name from Seveso II Directive: - not applicable -

category from Seveso II: - not applicable -

other hazards (1): - not applicable -

other hazards (2): - not applicable -

maximum quantity (tonnes): 0,009

use of substance as: STARTING MATERIAL

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: 0,009 **potential quantity:** 0,009

c) substance belongs to relevant inventory indirectly involved: No

actual quantity: -1 **indir_pot_quant:** -1

Source of Accident - Situation **country:** FA **ident key:** 1986_014_01

situation

industry

initiating event 2002 petrochemical, refining, processing

associated event - not applicable -

activity/unit

major occurrence 3102 process: chemical continuous reaction

initiating event 3102 process: chemical continuous reaction

associated event - not applicable -

component

major occurrence 4011 general pipework/flanges

initiating event 4011 general pipework/flanges

associated event - not applicable -

B Consequences Full Report

country: FA ident key: 1986_014_01

1 Area concerned

affected

extent of effects installation: Yes

establishment: Yes

off-site; local: No

off-site; regional: No

off-site; transboundary: No

illustration of effects - not applicable -

remarks In the Original Report there is no evidence of significant effects outside the e... see Appendix

Full Report B / area concerned - remarks

2 People

establishment popul. emergency personnel off-site population

total at risk 20

immediate fatalities

subsequent fatalities

hospitalizing injuries

other serious injuries

health monitoring

remarks No people were injured during the accident.

3 Ecological Harm

pollution/contamination/damage of:

- residential area (covered by toxic cloud) Suspected

- common wild flora/fauna (death or elimination) Suspected

- rare or protected flora/fauna (death or elimination) Suspected

- water catchment areas and supplies for consumption or recreation Suspected

- land (with known potential for long term ecological harm or Suspected

preventing human access or activities)

- marine or fresh water habitat Suspected

- areas of high conservation value or given special protection Suspected

remarks In the Original Report there is no evidence of significant ecological harms.... see Appendix

Full Report B / ecological harm

4 National Heritage Loss

effects on:

- historical sites not applicable - historic monuments not applicable

- historic buildings not applicable - art treasures not applicable

remarks No data available.

5 Material Loss

establishment losses off site losses

costs (direct costs to operator) (social costs)

in ECU ECU

material losses

response, clean up, restoration

remarks No significant material losses occurred except released isobutane and hydrogen f... see Appendix

Full Report B / material loss

6 Disruption of Community Life

establishment/plant evacuated disabled/unoccupiable destroyed

- **nearby residences/hotels** No No No

- **nearby factories/offices/small shops** No No No

- **schools, hospitals, institutions** No No No

- **other places of public assembly** No No No

interruption of utilities etc. no / yes duration

- **gas** No

- **electricity** No

- **water** No

- **sewage treatment works** No

- **telecommunications** No

- **main roads** No

- **railways** No

- **waterways** No

- **air transport** No

significant public concern none local level national level

- **off site populations** Yes No No

- **media interest** No No No

- **political interest** No No No

remarks In the Original Report there is no evidence of significant effects outside the e... see Appendix

7 Discussion of Consequences

C Response Full Report

country: FA **ident key:** 1986_014_01

1 Emergency Measures

taken - on site - not applicable - - not applicable -

- not applicable - - not applicable -

- not applicable - - not applicable -

- **off site** - not applicable - - not applicable -

- not applicable - - not applicable -

- not applicable - - not applicable -

still - on site - not applicable - - not applicable -

required

- not applicable - - not applicable -

- not applicable - - not applicable -

- **off site** - not applicable - - not applicable -

- not applicable - - not applicable -

- not applicable - - not applicable -

continuing contamination or danger

-on site not applicable

-off site not applicable

remarks - not applicable -

2 Seveso II Duties

pre-accident evaluation

Article item not due yet not done done/submitted evaluated

6 notification No No No No

7 policy (MAPP) No No No No

9 safety report No No No No

9, 10, 11 update No No No No

11 internal plan No No No No

11 external plan No No No No

13 informing public No No No No

9, 12 siting policy No No No No

post-accident evaluation

Seveso II duty was actual were actual compared with actual

contingency consequences consequences, the

addressed? addressed? predicted extent was?

Article item

7 policy (MAPP) not applicable not applicable not applicable

9 current safety report not applicable not applicable not applicable

11 internal plan not applicable not applicable not applicable

11 external plan not applicable not applicable not applicable

13 informing public not applicable not applicable not applicable

9, 12 siting policy not applicable not applicable not applicable

evaluation of safety organisation

organisational element element existed did element relate to actual circumstances of

yes / no no / partly / yes adequate?

- written policy objectives No

- specified management No

structure

- specified responsibilities No

- specified working procedures No

- specified procedures for No

assessment/auditing of

management system

- specified procedures for No

review and update of

management policy

- specified general training No

procedures

- specified emergency No

training procedures

evaluation of ecological impact control

organisational element element existed did element relate to actual circumstances of

yes / no no / partly / yes adequate?

- ecological status review No

before incident

- potential ecological No

consequences assessment

- ecological impact review No

after incident

- ecological restoration No

procedures

- subsequent review of No

restoration success

remarks - not applicable -

3 Official Action Taken

legal action

- not applicable -

other official action

- not applicable -

4 Lessons Learned

measures to prevent recurrence

After the accident, the provis... see Appendix Full Report C / lesson learned - prevent

measures to mitigate consequences:

Provision of automatic and/or ... see Appendix Full Report C / lesson learned - mitigate

useful references:

- not applicable -

5 Discussion about Response

- not applicable -

Appendices for the FA / 1986_014_01 report

Appendix Short Report / description of accident types:

ENVIRONMENT AND ATMOSPHERICAL CONDITIONS:

Moderate breeze blowed released gas away from the plant and nearby installations.

The leak occurred during normal refinery operation. Automatic detectors sensed the leak and sounded the alarm more or less simultaneously with a plant operator on patrol noticing it. He immediately confirmed the nature of the release to shift emergency controller who decided that in the short term a substantial release of LPG containing traces of hydrofluoric acid could not be avoided. After activating the emergency isolation and depressurisation procedures, he alerted the works fire team and lost no time in calling the local fire brigade to assist in the deployment of fire monitors which would deluge water into the affected area. Because of their familiarity with the plant and their long-standing liaison with the works fire team, the brigade had at least 20 monitors set up in record time. It was then a matter of maintaining water supplies while the plant could be depressurised sufficiently to allow temporary repairs. This critical stage lasted for about an hour. The flare stacks were used to vent down the alkylation plant. A moderate breeze blowed released gas away from the plant and nearby installations. Gas cloud diluted below the flammable limit within a few tens of metres

from the source of release.

Appendix Short Report / description of substances involved:

- Isobutane (C.A.S. CODE: 106-97-8): amount involved = 4,400 kg.

- Hydrogen Fluoride (C.A.S. CODE: 7664-39-3, E.E.C. CODE: 009-002-00-6): amount involved = 4.4*8.8 kg (0.1*0.2% concentration of Hydrogen Fluoride in Isobutane).

Appendix Short Report / description of immediate sources:

A leak occurred in an 8" bore steel pipe which formed one leg of an isobutane recycle stream. Flow through the pipe at the time of the leak was approximately 60,000 kg/h at a temperature of 84°C and a pressure of 15 barg. The isobutane contained residual amounts of hydrogen fluoride (0.1*0.2% by weight) carried forward from the reactor circuit.

Appendix Short Report / description of suspected causes:

INITIATING EVENT AND CONSEQUENCES:

A small corrosion hole (0.00019 m²) formed in the recycle pipe. The escaped gas

was immediately detected by automatic detectors and a plant operator.

CAUSES:

Examination of the ASME A106 (8" bore) x 8mm grade 13 steel pipe revealed that a plug of rust and sludge (containing 9.9% FeF₂, 8.1% FeF₃ and 37.5% Fe₂O₃) accumulated in base of a shallow bend. The retention of HF in this plug caused accelerated internal corrosion in a localized zone around the surface of the plug. The pipe formed part of the original installation which had been in use for about 5 years; generally corrosion was uniform and within the tolerances allowed for the recycle circuits of the plant.

Appendix Short Report / description of emergency measures taken:

INTERNAL TO THE ESTABLISHMENT:

The shift emergency controller activated the on-site emergency plan and alerted the works fire team and lost no time in calling the local fire brigade to assist in the deployment of fire monitors which would deluge water into the affected area. Because of their familiarity with the plant and their long-standing liaison with the works fire team, the brigade had at least 20 monitors set up in record time. It was then a matter of maintaining water supplies while the plant could be depressurised sufficiently to allow temporary repairs. This critical stage lasted for about an hour. The flare stacks were used to vent down the alkylation plant. Eventually a mechanical clamp was attached to the pipe to seal it.

EXTERNAL TO THE ESTABLISHMENT:

The off-site emergency plan was not activated.

Appendix Short Report / description of immediate lessons learned:

MEASURES TO PREVENT ANY RECURRENCE OF SIMILAR ACCIDENTS:

After the accident, modifications to prevent the accumulation of iron fluorides and oxides in recycle pipes were established. Details of these modifications and the reasons for them drawn to the attention of the plant designers.

MEASURES TO ALLEVIATE THE EFFECTS OF THE ACCIDENT:

After the accident, the provision of automatic and/or remote control on a number of valves to speed up isolation and depressurization procedures was established.

Appendix Full Report A / type of accident:

Owing to corrosion in an isobutane recycle piping system, a leak of isobutane containing traces of hydrogen fluoride occurred (code 1101). The gas cloud dispersed safely without igniting (it was diluted below the low flammable limit within a few tens of metres from the source leak).

Appendix Full Report A / dangerous substances:

The total establishment and the potential directly involved inventories of isobutane and hydrogen fluoride refer to the amounts released during the accident. The concentration of hydrogen fluoride in the isobutane stream varied between 0.1*0.2%.

Appendix Full Report A / source of accident - remarks:

The leak occurred in a 8" bore steel pipe (code 4011) which was one leg of an isobutane recycle stream. The recycle stream section (operating at 84°C, 15 barg) was a part of the Alkylation unit of a conventional oil refinery (code 2002). In the Alkylation unit, isobutane and butylene reacted in presence of a catalyst (hydrogen fluoride) to produce alkylates for motor spirit blending (code 3102). The isobutane contained residual amounts of HF (0.1 to 0.2% by weight) carried forward from the reactor.

Appendix Full Report A / causes of major occurrence:

The failure of the isobutane recycle piping (code 5102) was due to an internal corrosion. Examination of the pipe revealed that a plug of rust and sludge containing 9.9% FeF₂, 8.1% FeF₃ and 37.5% Fe₂O₃ had accumulated at the base of a shallow bend. The retention of HF in this plug caused an accelerated internal corrosion in a localized area around the surface of the pipe (code 5104). The possibility of this phenomenon was not identified during the process analysis (code 5307).

Appendix Full Report B / area concerned - remarks:

In the Original Report there is no evidence of significant effects outside the establishment because the gas cloud was diluted below the low flammable limit within a few tens of metres from the leak source.

Appendix Full Report B / ecological harm:

In the Original Report there is no evidence of significant ecological harms.

Appendix Full Report B / material loss:

No significant material losses occurred except released isobutane and hydrogen fluoride.

Appendix Full Report B / disruption of community life:

In the Original Report there is no evidence of significant effects outside the establishment.

Appendix Full Report C / lesson learned - prevent:

After the accident, the provision of automatic and/or remote control on a number of valves to speed up isolation and depressurization procedures was established.

Appendix Full Report C / lesson learned - mitigate:

Provision of automatic and/or remote control on a number of valves to speed up the isolation and depressurization procedures.