

Technical Briefing Note

The risk of ethylene decomposition in cross country pipelines

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This Technical Briefing Note (TBN) identifies what is considered by UKOPA to represent current UK pipeline industry good practice within the defined scope of the document. All information is guidance and should not be considered obligatory against the judgement of the Pipeline Owner/Operator. Where new and better techniques are developed and proved, they should be adopted without waiting for modifications to this TBN.

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CONTENTS

1.	Executive summary	1
2.	Objectives	2
3.	Risk of ethylene decomposition in pipelines	3
3.1	Background	3
3.2	Hazards	3
3.3	Causes	3
4.	Prevention / Mitigation	5
5.	Frequency of incidents causing loss of containment	6
6.	Risk analysis	7
7.	Conclusions and recommendations	8
8.	Ethylene decomposition theory and research	9
9.	Summary of literature	11
9.1	Protecting cavities from ethylene decomposition	11
9.2	Hot tapping of ethylene pipelines	11
9.3	Ethylene decomposition incidents	12
9.4	Other Incidents	16
10.	Relevant papers	17
10.1	List of Papers at the Symposium on Ethylene Decomposition held in May 1983 at Houston, Texas	17
11.	AGI Survey, Template (example)	18

1. EXECUTIVE SUMMARY

Ethylene decomposition is a risk to the safety and integrity of ethylene systems.

Under certain circumstances, dense phase ethylene can decompose to methane with release of heat and increase in volume. If this happens the pressure in a pipeline can increase, and if the flame front becomes static in the pipeline, there is a risk of over-heating the pipe wall. This could lead to the rupture of the pipeline.

This note explains the circumstances under which this could happen and summaries several background research papers. The precautions in place by UKOPA operators to reduce the risk of an ethylene decomposition are identified.

The risk of an ethylene decomposition occurring is also quantified with the precautions by UKOPA operators in place. It is calculated to be extremely low being almost 500 times less than the risk from 3rd party activity.

The possibility of decomposition is minimised by good design, engineering, maintenance procedures and protection systems. The risk of ethylene decomposition although low should continue to be considered in the design of new ethylene systems or modifications to existing systems.

Pipeline Emergency Response Officers PERO should be made aware of the potential of an ethylene decomposition being caused by an external effect and the necessity to mitigate this.

2. OBJECTIVES

The objective of this technical briefing note is to highlight the risks of the decomposition of ethylene in cross country pipelines, the potential effects and mitigations that can be put in place to reduce the risks.

3. RISK OF ETHYLENE DECOMPOSITION IN PIPELINES

3.1 Background

Ethylene decomposition can occur when dense-phase ethylene is subjected to high temperature such that it decomposes, usually to methane and carbon;



This is about one tenth the energy released when ethylene burns in air (-318 kcal/gm.mole). The adiabatic temperature rise from this reaction is reported to be 1330°C.

Decomposition is catalysed by oxygen and rust, and the higher the pressure, the lower the decomposition temperature. For 100 bar pure ethylene, the decomposition temperature has been quoted as low as 300-350°C, although other references quote a temperature above 500 °C. Under these conditions, the reaction front creeps slowly along the pipe with a velocity of approximately 0.3-1.0 metres/second; there is no likelihood of flame acceleration to detonation.

3.2 Hazards

Two main hazards arise from decomposition in pipeline systems;

- a) The risk that the flame front becomes static or very slow moving such that the forward velocity of ethylene matches the reaction front speed; the reaction front may then heat the pipe wall (above ~700°C required) causing rupture. This apparently occurred in the Arco incident, 20 August 1976 when ethylene decomposition developed within an above-ground 12-inch pipeline operating at 1320 psig.
- b) The decomposition front becomes trapped within a small isolated pipe system such that the pressure rise exceeds the burst pressure of the system. During the Arco incident, the operators shut a valve closing in the pig trap system and a thermocouple housing head blew off. Decomposition of dense-phase ethylene can produce high pressures in a limited volume system due to the high initial density of dense phase ethylene converting to gas-phase lower-density methane. However, localised expansion of the increasing gas volume would be absorbed in a long cross-country pipeline, so a dangerous significant pressure rise would not be expected to occur.

3.3 Causes

Four causes of high temperature in high pressure ethylene systems are;

1. Sudden compression of ethylene into a low-pressure system, especially a diatomic gas such as nitrogen. The pressure difference needs to be large (typically 60-80 bar) to cause the necessary compression-heating to set off the decomposition. Again, any oxygen present, or rust, can promote decomposition. Compression of ethylene into ethylene is less hazardous and is unlikely to cause the same degree of compression-heating.
2. Sustained external fire causing heating of exposed pipework containing ethylene, (especially static ethylene) can initiate decomposition.

3. Compressor malfunction (typically valve failure) causing ethylene to heat up in a compressor system.
4. Heater malfunction – heaters are sometimes used to raise the temperature of ethylene after leaving underground storage cavities.

4. PREVENTION / MITIGATION

A survey of UK ethylene terminals (2002) showed that extensive prevention systems have been installed for each of these causes to prevent a decomposition front developing and moving into the cross-country pipeline systems.

To prevent compression-heating, maintenance procedures require repeated nitrogen purging to remove any air before allowing low pressure pressurisation with ethylene, followed by slow pressurisation with ethylene up to operating pressure using small diameter by-pass lines fitted with suitably-sized orifice plates and manual isolation valves which limit the rate of pressurisation. Pressure-interlock systems are fitted such that automatic valves cannot be opened until the pressure has been equalised across the valves.

To avoid fires, AGIs are laid out to minimise risk of fire affecting ethylene pipework, and by minimising the number of flanges, fittings and valves. Gas detectors are located to identify leaks before ignition in the AGI compound, and fire detection and alarm systems shut off inlet and outlet valves from the compound.

Compressors are fitted with high temperature detectors and automatic remote isolation valves on compressor suction and delivery, actuated by high temperature in the ethylene systems to contain any decomposition within machine boundary. Cavities have rate of temperature rise alarms and high-speed trip valves.

For ethylene heaters, use of heating medium which is unable to exceed decomposition temperature, lower tube-skin temperatures, reliable temperature measurement and trip systems in the heater exit stream, low flow detection and trip, have eliminated or minimised the risk.

No hot-tap activities are allowed on ethylene pipelines.

5. FREQUENCY OF INCIDENTS CAUSING LOSS OF CONTAINMENT

Several incidents were recorded in the USA during the 1970s, the most notable of which was the Arco incident in 1976. Following this, a Symposium on Ethylene Decomposition was held in May 1983 in Houston, Texas; several UK operators attended. Various recommendations from the symposium resulted in the prevention methods outlined above.

Recorded incidents involved external fires, compressors, heaters and driers, and all involved above-ground pipework and equipment – there appear to have been no incidents involving underground pipework. One paper discusses the probability that quenching of the reaction occurs due to heat transfer once the reaction front moves into underground pipework.

Refer to the appendices for further details of historic events.

6. RISK ANALYSIS

Fires in ethylene terminals are very infrequent. Over the years since 1960 there have been approximately 25 AGIs in operation for a total of approximately 500 operating years. Assuming, say two fires have occurred in the past with the potential to initiate decomposition, an incident rate of 1 in 50 years (0.02 per year) may be realistic.

Rapid manual operation of large valves with the potential to cause decomposition has been eliminated as far as possible, but there may still be a human element which could result in an error allowing decomposition.

Assuming 1 such incident could occur at one of the operating terminals every 25 years (i.e. a conservative figure lower than the average life of a terminal to date), the frequency is 0.04 per year.

Compressors and driers are only in use at a few of the AGIs, so the risk of a decomposition incident is low, say 1 in 100 years or 0.01 per year.

The frequency of an initiating event is therefore $0.02 + 0.04 + 0.01 = 0.07$ per year.

With extensive protection and mitigation systems in place, the risk reduction achieved is assumed to be a factor of at least 100 – i.e. frequency reduction by 0.01.

The risk of an initiating event reaching one of the cross-country pipelines is therefore 7×10^{-4} per year.

Finally, to cause pipeline rupture, the pipeline flowrate has to be such that the reaction front becomes static or very slow moving, so the forward velocity has to be between 0.3 and 1.0 metres /second, and the reaction front must not be quenched in the underground section.

Assuming a probability of 0.1 for these, the overall frequency of a rupture is 7×10^{-5} per year. This compare with ~0.03 per 1000 km.years for 3rd party activity causing rupture or 3×10^{-2} per year for the 1000 kilometres of ethylene pipelines currently in operation – a factor of nearly 500 times higher.

7. CONCLUSIONS AND RECOMMENDATIONS

The risk of decomposition causing pipeline rupture in an ethylene cross country pipeline is considered very unlikely (and may not, in fact be possible). The frequency is ~ 500 times lower than for 3rd party activity.

Like other failure mechanisms such as overpressure and fatigue which are under the control of the pipeline operator, the possibility of decomposition is minimised by good design, engineering, maintenance procedures and protection systems.

Consideration should also be given to the threat of thermal decomposition arising on an ethylene system due to external effects such as a fire. Mitigation to prevent impingement of a flame or to cool the pipeline may be required.

The pipeline emergency response officers (PEROs) should be made aware of the decomposition potential on an ethylene pipelines and the need to mitigate heating of the ethylene, removal of heat sources, or heated ethylene and other potential effects.

8. ETHYLENE DECOMPOSITION THEORY AND RESEARCH

There are a number of the original references used in the historical study that were contained within an ICI library that unfortunately was destroyed. The original documents are no longer available however a summary of the findings where documented is retained.

- **Decomposition in Compressed Ethylene, R K Laird, 3 December 1951 *No longer available.***

Earliest references are to work carried out to determine ethylene decomposition under conditions developed for polyethylene manufacture of 250 atmospheres (3765 psig). Experiments using an electrically heated wire showed there was a critical ignition temperature for specific ethylene pressure and temperature conditions which would cause local decomposition to carbon, hydrogen and methane. For some conditions the decomposition spread to the whole contents of the 80 cc bomb, and this was found to be dependent on the starting gas temperature, which also needed to be above a critical value. Also tests up to 1600 ats showed that the critical wire and gas temperatures decreased as the pressure increased.

Figure 2 is of particular interest (and later mis-quoted) – it plots ethylene pressure against temperature showing safe and explosive regions and starts from zero on each axis.

It appears to suggest that for 80-100 ata ethylene, the decomposition temperature is 340°-360°C.

- **The Explosive Decomposition of Compressed Ethylene, R K Laird, 13 February 1959, Alkali Division, Northwich Research Report X 181/32/38. *No longer available.***

This is an ICI report which describes in much more detail the work carried out between 1950 and 1952. It was a factual record of earlier experimental work which had not previously been fully written up. It is more concerned with minimum ignition energies and other parameters, although it does report work carried out at 100 ats. Fig 6 indicates that at 100 ats the propagation / no propagation boundary is in the 350°C region.

- **The Thermal Decomposition of Ethylene, WW Lawrence and S E Cook, Ethyl Corp, Baton Rouge.**

Published paper, believed to be 1969, examines temperature, pressure and pipe diameter as parameters affecting thermal decomposition of ethylene.

- **Decomposition of Ethylene Under Pressure – Literature Review, F Rowe, HOC Research and Development Department, 2 December 1969. *No longer available***

This is the first of a number of papers considering the possibility of hot-tapping on the TPEP. It discusses the possibility of further investigating the hazards of ethylene decomposition by commissioning work at the Atomic Weapons Research Establishment.

- **Ethylene Pipeline Hazards – F Rowe, 4 May 1977 *No longer available.***

Plot of points of pressure and temperature where decomposition has been reported.

- **The Pressuring up of Ethylene Lines, S G McLoed, BP Chemicals, Grangemouth, 1977.**

Recommends compression times for pressuring up ethylene systems, includes calculations of compression.

- **Ethylene Decompositions, D J Lewis, 29 Oct 1979 *No longer available.***

Exposition by David Lewis, the ICI Mond Division combustion expert, on the state of knowledge on ethylene decomposition in 1979.

- **Decomposition of Ethylene Under pressure: Review, F Rowe, ICI Petrochemicals Division, 3 July 1980 *No longer available.***

Comprehensive review of literature on the exothermic decomposition of ethylene under pressure, with special reference to the safety of pipelines and storage operations.

- **Spontaneous Ethylene Decomposition Temperature: The Birth of a Legend, F Rowe, March 1982, *No longer available.***

Note for file which casts doubt on the understanding that the minimum decomposition temperature of ethylene is 315 C at 60 bar.

- **Decomposition Flame Propagation Limits of Ethylene and Mixtures with Other Gases, Lawrence G Britton, Process Engineering, Union Carbide Corp, USA, Process Safety Progress (Vol 15, No 3), 1996.**

This is an up-to-date exposition of the state of knowledge of ethylene decomposition, although the paper covers ethylene-oxygen and ethylene- hydrogen mixtures as well and is particularly interested in decomposition of these mixtures in purifier beds (Carbide operate ethylene oxide plants which have guard beds on the ethylene supply line). As a result, it is difficult to define which results apply to high pressure ethylene pipeline systems.

9. SUMMARY OF LITERATURE

9.1 Protecting cavities from ethylene decomposition

- **A System to Protect Ethylene Storage Cavities from Decomposition Reactions, Richard C Swanson, Shell, USA.**

This paper was presented at the Symposium on Ethylene Decomposition, Houston Texas, May 1983, and describes Shell system for high temperature detection and automatic reverse acting gate valve to stop a decomposition front entering a storage cavity.

- **Stratton Ridge Salt Dome Storage for No 1 Olefins Facility- Amoco Chemicals Corporation, 3/8/73.**

Discussion of design considerations to avoid decomposition, particularly relating to the heaters. Included as an attachment is the Explosibility of Ethylene Report from Amoco, HRC report No 3170.

- **Project 4959 - Ethylene Storage at Holford – Design Philosophy for Temperature Detection of an Ethylene Decomposition 11 August 1981 *No longer available*.**

This report describes the design philosophy for the rate of temperature rise detectors installed at Holford.

- **Note, Project 4959 – Adiabatic Compression in Borehole Instrument Tube, J S Edgley. *No longer available*.**

Discusses concern that instrument tube failure could initiate ethylene decomposition.

- **Ethylene decomposition – Note by D K Holliday *No longer available*.**

Discusses points when Plastic and Petrochemicals merged in ICI. Also has computer print-out of initial and final pressure and temperature of ethylene decomposition.

9.2 Hot tapping of ethylene pipelines

1. How to safely hot tap ethylene lines. Dave J Hicks, T D Williamson inc, Tulsa, Oil & Gas Journal Jan 15, 1979.
2. Ethylene behaviour Related to Hot Tapping. W B Howard, Monsanto Co, St Louis, USA, CEP Technical Manual, 1975, also paper presented at 79th National Meeting, Houston Texas, March 1975.
3. Hot Tapping of Ethylene Pipelines. No longer available. T A Kletz letters to and from J H Burgoyne and Partners, and A L Cude, 1973- 1974.
4. Monsanto view of hot tapping on pipelines containing ethylene. No longer available. T A Kletz from Walt B Howard.
5. Ethylene behaviour Related to Hot Tapping, W B Howard, Monsanto Co, St Louis, USA, 1972 version of paper.

6. Welding of Ethylene Under Pressure – consideration of Esso Proposal A L Cude and T A Kletz, 1972. *No longer available*
7. Hazards of Explosive Decomposition of High-Pressure Ethylene in Pipelines. A L Cude 19/5/70. *No longer available*
8. Suggested programme for investigation of the possible hazards of the external fusion welding of pressurised ethylene pipelines, R D Rowe. *No longer available*
9. Letters warning of risks of welding on live ethylene lines S A Lamb and M E Pool 1968. *No longer available*

9.3 Ethylene decomposition incidents

9.3.1 [Arco incident, 20 August 1976](#)

Dave J Hicks, T D Williamson inc, Tulsa, Oil & Gas Journal Jan 15, 1979.

Ethylene Pipeline Rupture, Report by John T Shelton, Arco, 2 September 1976. Report of the investigating committee into the ARCO incident 1976.

Summary of Conditions / Effects of Ethylene Decomposition Caused by sudden compression of air/ethylene or nitrogen ethylene mixtures.

An ethylene decomposition developed within a 12-inch pipeline metering run following maintenance and propagated into a 12-inch pipeline containing flowing ethylene at 1320 psig. After the trailing edge of the decomposition flame front stabilized and heated the pipeline sufficiently, the pipe weakened and ruptured, releasing the ethylene which promptly ignited.

The decomposition was caused by sudden compression of air and ethylene from atmospheric to 1320 psig in the closed-in metering run.

The 6-inch incoming line and 12-inch outgoing line initially had 13.73 tonnes per hour of ethylene at 1320 psig flowing through. The 12-inch line from the metering run was isolated and de-pressured to atmosphere to remove the orifice box for maintenance. A gap of 2 feet (60 cm) was left open to atmosphere for about 30 minutes. After re-installation of the orifice box, the limit switches were being checked on one of the MOVs. The inlet MOV to the 12-inch meter run was opened fully and there was a surge and rushing sound as ethylene filled the meter run. The operators noticed that gases were escaping from the thermocouple head in the meter run. To contain the leak, the MOV was closed. And at this point the explosion-proof head on the thermocouple housing blow off. A pulsating flow of soot-like smoke blew out of the thermocouple well. 3-4 minutes later, operators noticed heat radiation and paint starting to bubble on the 12-inch line downstream of the pig trap which is 90 feet (27 metres) from the meter run. They requested the pipeline to be blocked in and observed the reverse bend beginning to push out of the ground (from thermal expansion) and evacuated the area. A short time later the line ruptured.

Later, the meter run was found full of fluffy soot, and carbon was found downstream in the 12—inch line. However, no carbon was found in the attached 8-inch by-pass line attached to the meter run which goes directly into the ground and indicates that the flame does not travel downwards easily. It appeared that heat effects were dissipated by both convection to the air and conduction to the ground.

The point where the pipe ruptured showed thinning of the metal and a longitudinal split. The temperature at this point is estimated to have reached 700-800°C. Carbon was found in the 6-inch incoming line, and at least 80 metres downstream the rupture in the 12-inch line. It appeared the decomposition front proceeded primarily downstream in the flowing pipeline. Paint blistering occurs at 200°C which is the calculated flame equilibrium temperature as it was cooled in the pipe.

9.3.2 [Ethylene fire at EVC metering compound, 13 May 1999](#)

From incident report by W A Holmes.

A leak of high-pressure ethylene was caused by removal of a turbine meter sensor probe which broke into the pressurised system. This caused injury to the instrument technician who removed it, and a subsequent explosion and fire. The fire was allowed to burn out after effective isolations had been made. Evidence of decomposition in pipelines adjacent to the fire was apparent after the incident, with paint blistering on the top of the affected pipelines, and carbon inside the pipes.

The instrument technician was unaware that he was breaking into the pressurised system when he removed the sensor probe. A number of people heard the initial gas release and saw the white cloud generated. Estimates of around 10 seconds between the initial release and the cloud exploding are typical. A visitor approaching the plant reported that he saw the flame propagate from within the compound to the edges of the cloud.

10 minutes after the initial gas release, the pressure in the metering skid had fallen to 10 barg. The flame had stabilised and was burning without a (smoke) plume. The fire finally put out 1 hour 52 minutes after the initial release.

Gas detectors in the compound alarmed at 14.34.35, and the inlet and exit isolations valves V25 and V19 were manually activated and closed from the VC control room at 14.36.15 and 14.36.18 respectively.

The decomposition was contained by the isolations made within the compound.

9.3.3 [Ethylene pipeline incident, Shell, Berre, France, 30 May 1991](#)

Note for file, F J Adams

The incident occurred on a section of the Trans-ethylene pipeline where it leaves Shell's factory. It ran above ground across the site before going underground at a street crossing near the factory boundary. At 10.00 am, a leak occurred on the pipeline just after the point where it went underground. The leak was situated near the street which ran along under the main pipe-bridge supporting many pipes including an insulated HP ethylene line which went from the naphtha cracker to the adjacent consuming plants.

Due to wrong information, the fire brigade closed off the street at one end with 2.5 minutes. However, the other end of the street was open, and this allowed a contractor's lorry to pass through the vapour cloud. The lorry stalled, and in trying to re-start the driver ignited the vapour cloud. The cloud ignited, and the leak formed a torch flame. This flame impinged on the pipe-bridge and heated the HP ethylene line on the bridge. This 6-inch line carried liquid ethylene at 60 barg. At the time the line was static and blocked in. After 8 minutes this line exploded. The upper part of the pipe-bridge collapsed allowing lines to bend and rupture. The flame

from the burning collapsed ethylene pipeline impinged on the above ground section of the Trans-ethylene pipeline. The ethylene transfer in this line had been stopped using remotely operated emergency shutdown valves, but the lines was still pressurised up. After 15 to 20 seconds this ethylene line also exploded and ruptured. Approximately 100 metres of this line whiplashed about and the flaming end ignited a nearby SBR rubber warehouse setting alight 2,000 tones of rubber.

9.3.4 [Esso Sarnia – Ethylene drier explosions](#)

Rupture of an ethylene drier exit line due to flame impingement 4th April 1970.

An explosion occurred in a 3-inch ethylene drier outlet manifold at 700 psig when it was overheated by flame impingement from a large flange fire and ruptured. The outlet line normally operated at 35°C so was well below decomposition temperature. The burst line was un-insulated, and there was no flow through the line at the point where the failure occurred. The large flange fire was 2 metres from the burst, and the arrangement was such that flame impingement had occurred. The leaking flange had been discovered burning with a small flame shortly before the line failed, the small flange fire was extinguished, and pipe fitters were summoned to tighten the flange. Before they arrived, the flange leak suddenly got worse and ignited. The 3-inch line burst shortly afterwards. It was not clear whether line rupture was caused by loss of tensile strength due to overheating, or excess internal pressure resulting from ethylene decomposition.

Rupture of ethylene drier exit line due to overheating 14th November 1971.

The 3-inch hot outlet line from the drier regeneration salt bath heater containing ethylene at 1000 psig ruptured without warning. The resulting large fire was quickly extinguished by isolating the system. The line rupture explosion which was heard 5 miles away. The sudden line rupture was caused by ethylene decomposition within the line, probably due to excessive fuel gas firing of the salt bath heater due to TRC failure. No safety devices were provided to protect against over-firing, and consequent overheating of the high-pressure ethylene led to decomposition.

9.3.5 [Low level ethylene decomposition – An inconvenience or a warning?](#)

S G Bowen, Exxon Chemical Co, USA, IChemE symposium series No 80, 29 March 1983.

Exxon experienced an occurrence of low-level decomposition in 1982 when for no apparent reason, an ethylene heater in a relatively remote location was unable to maintain its required outlet temperature. When the heater was inspected it was found to be fouled with black sticky material.

9.3.6 [Ethylene and dryer compressor incidents - Explosive decomposition of ethylene – Exxon's experience](#)

E C Sommer, 1970s.

This note describes 6 incidents in Exxon's operations where explosive decomposition has been suspected.

An ethylene compressor exploded as a result of suspected ethylene decomposition induced by improper installation of 2 discharge valves at the second stage. These valves were

interchangeable and were not marked or keyed to show the direction of flow. Normal operating conditions on the discharge side were 1500 psig and 120°C. The incorrectly valves generated much high local hot-spots.

About 8 minutes after starting up a reciprocating ethylene compressor, a violent explosion occurred. A piece of the discharge bottle, weighing 20 kilograms, landed 150 metres away after passing over 5 tanks. Another piece of metal landed 250 metres away. The compressor had been started up against a closed discharge valve and there was no safety valve protection. Investigation showed strong evidence of ethylene decomposition.

Within hours of start-up, the aftercooler of a reciprocating ethylene compressor exploded. Investigation concluded that ethylene decomposition occurred in the head end of the second stage cylinder, propagating down the 3-inch discharge line into the air-cooled aftercooler.

A reciprocating ethylene compressor has been operating with bad suction valves on the second stage cylinder and was scheduled to be shut down. The operators noticed that the first stage discharge temperature was 150°C instead of the normal 120°C. Shortly afterwards, they noticed paint blistering and smoking on the first stage discharge manifold. While shutting down the compressor, a gasket leak and fire occurred. Investigation showed strong evidence of ethylene decomposition.

A 3-inch manifold on an ethylene dryer exploded. Flame impingement had occurred as a result of a small flange fire. Metallurgical examination indicated failure was due to sudden pressure rise such as from an internal explosion rather than from overheating and loss of stress.

The outlet line from an ethylene salt bath heater exploded violently. The explosion was heard 5 miles away. It is thought that the salt bath was overheated to about 600 F due to malfunctioning of the temperature controls. Normal operating conditions were 1100 psig and 450-500 F.

9.3.7 [Enjay Chemical Company, C180C aftercooler decomposition and rupture.](#)

Report of Investigating Committee June 12, 1970.

Ethylene purge compressor sustained an ethylene decomposition in the head end of the second stage cylinder. Decomposition propagated down the 3" discharge line into the compressor after-cooler where it detonated causing a violent explosion which destroyed the after-cooler. A small fire following the detonation was readily extinguished. No personnel injuries. Comprehensive investigation report.

9.3.8 [Enjay Chemical Company, C100B primary compressor fire.](#)

Report of investigating committee December 20, 1968

An ethylene fire occurred on the first compression stage, shortly afterwards, a severe leak occurred developed at the first stage flange. The fire was extinguished after about 25 minutes. Probable cause was abnormally high temperature on the first stage delivery. First stage cylinder showed evidence of ethylene decomposition.

9.3.9 Compressor decomposition incidents

Survey by J J Glanville of ICI and other incidents for the Polythene Group Conference 1972. Total of 7 incidents reported.

9.3.10 Explosion at Dow's Freeport LDPE unit November 1981

6 people were killed in this explosion. Cause was traced to re-pressurisation of separator. About 3 hours after the separator was re-pressurised, the 3" outlet pipe on the bottom ruptured causing a release of ethylene. An explosion and fire resulted which killed 6 men.

9.4 **Other Incidents**

9.4.1 Heater incidents

An incident occurred on a cavern storing ethylene in which a man was killed (1978). The system was at 1100 psig and ethylene decomposition started in the drier and moved into the inlet ethylene pipe. The decomposition stabilised at a point where the propagation velocity equalled the flow velocity. This caused the pipe to burst at this point. A black product called "rouge" was found in the line after the incident. The drier was not fitted with relief devices.

Prior to entering the driers on the regeneration cycle, ethylene was heated by being passed through a tubular heater where the ethylene pipes are immersed in a gas-fired eutectic salt mixture, and then through the wet desiccant bed. The gas leaving the bed being dried is compressed and returned to the salt cavity. The flow of ethylene stopped through the heater, but the heater was left operating with 1200 psig ethylene in it. This caused a thermally-initiated ethylene decomposition inside the heater with the result that the pipes outside the heater unit ruptured. Carbon was found in the desiccant bed.

9.4.2 Cavity incidents

An incident occurred in 1955 with an ethylene storage well which contained about 10,000 to 20,000 tonnes of ethylene. The cavity was overfilled and the change in pressure on the brine line under such conditions had not been foreseen. The brine line fittings were of cast iron on the well head and when the overfilling occurred, the fittings failed, and ethylene escaped and ignited. The well head was in a ground pit, and 2 men who were in the pit at the time of the incident were burnt and killed. All the ethylene in the cavity was lost in the ensuing fire. The radiation from this incident indicated that a safety zone against radiation from the fire of about a square mile would be required.

A storage well lost the whole well head assembly under LPG (propane) storage conditions in 1972-4 (date uncertain). About 9000 tonnes of gas were vented out over a long period through an 18-inch orifice and did not ignite. Gas was smelled 7 miles away.

10. RELEVANT PAPERS

10.1 List of Papers at the Symposium on Ethylene Decomposition held in May 1983 at Houston, Texas

1. Theory of Ethylene Decomposition, G R Worrell, Arco. G R Worrell's has published articles from Hydrocarbon Processing 1977 and 1979.
2. Laboratory and design evaluation of ethylene decomposition related to underground storage. R A Mancini, Amoco, comprehensive study of possible effects of decomposition in a cavity.
3. Research Studies involving decomposition, G R Worrell. Arco.
4. Possible Ethylene Decomposition in a Steam heater, D G Bowen, Exxon.
5. A Case History of an Ethylene Decomposition in a Pipeline. F F McKay Arco, Good description of the Arco incident.
6. Decomposition incidents in an ethylene drier system. D G Bowen, Exxon.
7. A System to Protect Ethylene Storage Caverns from Decomposition Reactions. R C Swanson. Shell Development Company.
8. Texaco Company Handling and Storage of Ethylene. C Helbring, Texaco inc.
9. Safety Features for Underground Storage of Ethylene. D G Worrell, Arco.
10. Safety Features for Underground Storage of Ethylene Flame arrestor design. G N Bogel. Arco.
11. Safeguarding high pressure driers from Ethylene Decomposition. C J Kuhre, Shell Oil Company.
12. Potential for Decomposition with Ethylene Compressors and Preventative Measures. E F Carmody, Dow Chemicals USA.
13. Decomposition in Polyethylene Process Plants. R A Walker, Gulf Oil Chemical Company.
14. Safe Commissioning of Pipelines and other equipment. J E Arbour, Dow Chemical USA.
15. Commissioning of Texas-Louisiana Ethylene Pipeline. F F Fischer, Shell Pipe Line Corporation.
16. Conversion of well storage from LPG to Ethylene. G W Liefer, Diamond Shamrock Corporation.
17. Special Precautions for Hot Tapping High Pressure Ethylene Equipment. J W Fraser, Dow Chemical USA.

11. AGI SURVEY, TEMPLATE (EXAMPLE)

A template that could be used to review the risk of decomposition at an ethylene AGI.

Name	
Location	
Pipeline(s)	
AGI Purpose	
Potential for fire impingement • flanges – how many and direction • vents • seals / drains • local areas	
Potential for pressurisation • is pipeline pressurised from here? • what with • how often? • why? • by whom?	
Potential for heating • is there a possible ethylene heating mechanism? • driers, compressors, heaters?	
Safeguards – fire impingement • minimise flanges? • welded in valves • flange jet fire impingement possible? • leak detection – to where? • fire detection – response? • temperature detection – what and to where?	
Safeguards – compression • mechanical interlocks? • instrument interlocks? • how is it pressurised? • procedures, warnings, precautions, rate of pressurisation • nitrogen source / contamination	
Safeguards – heating • temperature trips / alarms? • potential recognised	

Isolation facilities / flow limitation - remotely operated valves? - where are they actuated from? - response time adequate?	
Procedures - warnings about decomposition? - training / instructions	