STYRENE GAS LEAK

"Styrene being a toxic chemical, it should be handled by observing all safety measures"

- **R. Rajasekharan Nair**

INTRODUCTION

Today, all our efforts are diverted to contain the spread of COVID-19. To fight against COVID-19 Pandemic, our country has resorted to the lockdown procedures which began on 25th March, 2020. The COVID-19 Lockdown period was extended thrice and now we are in the fourth phase of lockdown, which will end on the 31st May, 2020.

During the lockdown period, almost all the economic activities of the country were stalled. However, in phase 3 of the lockdown, some relaxations were given to resume selected production activities especially in Micro, Small and Medium Establishments (MSME) units. The *LG Polymers India Private Limited (LGPI), Visakhapatnam*, is one among the few units who wanted to resume the production, after a gap of 40 days COVID-19 induced lockdown. Accordingly, the plant started its maintenance activities and during this process, the Styrene gas leaked from the plant in the early hours of 7th May, 2020. The styrene vapour spread over *R.R. Venkatapuram* and four other villages of *Visakhapatnam* in a radius of 1.5 to 3 KM. After inhaling the styrene gas, 12 persons died and more than 300 were hospitalised, out of which the condition of 20 were critical, requiring ventilator support. Due to this tragedy, more than 2000 residents had to be evacuated from areas in the vicinity of the *LGPI*.

Incidentally, no employee of *LGPI* was injured in this accident. Since no factory employee was injured, probably, it may not be treated as an industrial disaster under the purview of the *Factories Act of India, 1948*. Nevertheless, it should be treated as one of the major chemical accident in India, in recent years, though its severity and impact is much less than that of *Bhopal Gas Leak*, which had occurred about 37 years ago. Probably, had the COVID-19 Pandemic was not there, this accident would have drawn more attention than the present, because presently the people are more worried about the spread of Coronavirus and its higher strikes down rate.

As the styrene gas leak at *LG Polymers India Private Limited* is a major chemical disaster, this article is focused on the potential health hazards of styrene and preventive measures to be adopted to mitigate the recurrence of similar accidents in future.

THE CHEMICAL INVOLVED

The chemical involved in the *Visakhapatnam* gas leak was Styrene (C_8H_8). Styrene, a petroleum by-product, is the primary raw material from which polystyrene is made. The physical properties of Styrene are given in ***Table 01.***

Styrene was discovered in 1831. However, it did not become commercially important until 1942 when it was used in the synthesis of unsaturated polyesters and reinforced plastics. Styrene, first commercially produced in the 1930s, played an important role during World War II in the production of synthetic rubber. After the war, much of the use of styrene shifted to the manufacture of commercial polystyrene products.

The method mostly used for the industrial production of Styrene involves the catalytic dehydrogenation of Ethylbenzene at 500 – 700 ^{O}C and 30 mg Hg. Ethylbenzene ($C_6H_5C_2H_5$) is a colourless liquid with a strongly irritant smell. It is used on a large scale as a raw material or intermediate in organic synthesis, in particular in the production of styrene and synthetic rubber. The catalysts are mixtures of Zinc Oxide (86%) Aluminium, Calcium, Magnesium, etc.

Styrene is used in everything from food containers and packaging materials to cars, boats, computers, and video games. Styrene is the precursor to polystyrene and several copolymers.

Styrene is employed in the manufacture of a wide range of polymers (polystyrene) and copolymers elastomers such as Butadiene – Styrene rubber or Acrylonitrile Butadiene – Styrene (ABS) that are obtained by the copolymerisation of Styrene with 1-3 Butadiene and Acrylonitrile. The Styrene is widely used in the production of polyester resins, in particular transparent plastics. Styrene is also found in vehicle exhaust, cigarette smoke, and in natural foods like fruits and vegetables.

Some of the leading producers of styrene in the world are: *Americas Styrenics, Carville Styrenics Complex, Ineos Nova, LyondellBasell, Pars Petrochemical Co, Tabriz Petrochemical Co, Jubail Chevron Phillips Co, Shell Chemicals Canada Ltd, Integrated Refinery and Petrochemical Co, Siam Styrene Monomer Co, Saudi Petrochemical Co, Honam Petrochemical, LG Chem Ltd, Samsung Total Petrochemicals Co Ltd, Formosa Chemicals and Fibre Corp, Mitsubishi Chemical Corp, Sinopec Beijing Yanshan Petrochemical Co Ltd and Daqing Petrochemical Co.* However, in *India*, there is no producer of styrene and the demand is being met by imports.

Table 01: Physical Properties of Styrene

Synonyms and Trade Names	Styrene Monomer, Vinyl Benzene, Phenylethene, Phenylethylene, Cinnamene, Styrol, Diarex HF 77, Styrene, Styropol
Appearance	Colourless Oily Liquid
Odour	Sweet, Floral
Molecular Formula	C_8H_8 ($C_6H_5CH=CH_2$)
CAS Number	100-42-5
UN Number	2055
Molecular weight	104.15 g/mol
Specific Gravity	0.91
Melting Point	−30 °C (−22 °F)
Boiling Point	145 °C (293 °F)
Vapour Pressure	10 mm Hg (30.8 °C)
Flash Point	32.3 °C
Explosive Limit	1.1 - 6.1 %
Ignition Temperature	490 °C
Solubility	Ethanol, Ethyl Ether, Ketones
	Insoluble in water
	Dissolves Organic Substances and Polymers
Exposure Limits	
TWA (OSHA)	100 ppm (426 mg/m^3)
TLV (ACGIH)	50 ppm (213 mg/m^3)
STEL (ACGIH)	100 ppm (426 mg/m^3)
IDLH	5000 ppm
MAC (USSR)	5 mg/m^3

Reactive Potential

The existence of the double bond in the Vinyl group gives Styrene great reactive potential. It readily undergoes hydration, oxidation, halogenation or polymerisation, especially in the presence of heat, or light, and it is a common practice to add 3% Hydroquinone to Styrene to inhibit polymerisation during storage or transport.

Styrene polymers easily upon heating above 65^{O}C causing fire and explosion hazards. It reacts violently with strong oxidants. Due to low electric conductivity, the substance can generate electrostatic charges as a result of flow, agitation, etc. It should be stored in a flameproof, cool, well ventilated area separated from oxidants.

THE ACCIDENT

Styrene gas leak was occurred at the plant of *LG Polymers India Private Limited, Visakhapatnam, India*, on the wee hours of 7th May, 2020, killing 12 persons and injuring more than 300 ***(See Fig 01, 02, 03 & 04)***.

Fig 01: LG Polymers India Private Limited –Visakhapatnam plant

Fig 02: Victims in the hospital

Fig 03: Victims lying on the road side

Fig 04: Victims lying in the Gutter

Incidentally, *LG Chem Ltd (South Korea)* has a very strong presence in Styrenics business in *South Korea* and have plans to establish an equally strong presence in Indian market. It considered *India* as an important market and in its aggressive global growth plan identified *Hindustan Polymers* as a suitable company for entering Indian market through 100% takeover.

The *Hindustan Polymers* was a company established in 1961, for manufacturing Polystyrene and its Co-polymers at *Visakhapatnam*, *India*, which was taken over by *LG Chem Ltd (South Korea),* and was renamed in July, 1997, as *LG Polymers India Private Limited (LGPI)*. Presently *LGPI* is one of the leading manufacturers of Polystyrene (PS), Expandable Polystyrene (EPS) and Engineering plastics Compounds (EPC) in India.

Immediately after the gas leak, there was a hue and cry all over the country over the safety lapse on the part of *LG Polymers.* Thus, the *Government of India* deputed a study team consisting of *Dr. Anjan Ray, Director, Indian Institute of Petroleum, Dehradun* and *Dr. Shantanu Geete, Styrene Expert from Supreme Industries Ltd., Mumbai* to investigate the accident and submit a report. Accordingly, the two experts, submitted their preliminary report to the Central and State Governments on 10th May, 2020. The details of the report are yet to be known.

In the meantime, an expert of the plant, revealed that in the early hours (3:37 am) of 7th May, 2020, styrene vapours leaked from one of the two storage tanks in the plant. According to him, the leaked storage tank has a capacity of 2400 MT, but contained only about 1800 MT of styrene monomer. As some of the portion of the tank was empty, there were enough room for the formation of vapour inside the tank. As the quantity of the vapour began to increase, the tank started to behave like a pressure cooker. When the pressure rose beyond control, the safety valves opened, allowing the vapour to find its way into the atmosphere. The expert who had led a team in the containment operation also said that had the safety valves not functional, at the right time following the gas leak, the tank would have eventually exploded due to high pressure, killing many more people.

It is believed that, as the plant was closed for over 40 days due to the COVID-19 Lockdown, there was a variation in temperature between the bottom and upper parts of the storage tank. This variation in temperature might have led to self-polymerisation inside the tank, which in turn formed the formation of vapours inside the tank.

In the meantime, *National Green Tribunal (NGT)*, which ordered *LG Polymers* to pay Rs. 50 crores as interim compensation for the gas leak and setup a 5-member fact finding committee to inquire into the incident leading to the death of several innocents. As ordered by *NGT*, the company had already deposited Rs. 50 crores with the district magistrate.

POTENTIAL HAZARDS

Styrene and ethylbenzene poisoning are very similar. Styrene may enter the body by both vapour inhalation and being liquid soluble by absorption through intact skin. It rapidly saturates the body in 30 – 40 mins is distributed throughout the organs and is rapidly eliminated (about 85% in 24 hours) either in the urine (about 71% in the form of oxidation products of the Vinyl group (hippuric and mandelic acids) or in the expired air (10%).

The presence of the double bond in the side chain of styrene significantly increases the irritant properties of the benzene ring; however, the general toxic action of styrene is less pronounced than that of ethylbenzene. Liquid styrene has a local effect on the skin. Animal experiments have shown that liquid styrene irritates the skin and causes blistering and tissue necrosis. Exposure to styrene vapours may also give rise to skin irritation.

Acute Poisoning

Vapour of styrene in concentrations of over 2 mg/m^3 may cause acute poisoning in laboratory animals, the initial symptoms being irritation of the mucous membranes of the upper respiratory tract, the eyes and mouth. These symptoms are followed by narcosis, cramps and death due to respiratory – centre paralysis. The main pathological findings are oedema of the brain and lungs, epithelial necrosis of the renal tubules and hepatic dystrophy.

Styrene is toxic by ingestion. Animal experiments have shown that digestive absorption of styrene causes symptoms of poisoning similar to those resulting from inhalation. Lethal doses are as follows: 8 g/Kg body weight for styrene and 6 g/kg for ethylbenzene; lethal inhalation concentration is between 45 and 55 mg/l

In industry the danger of acute styrene poisoning may occur as a result of a breakdown or faulty plant operation. A polymerisation reaction that gets out of control is accompanied by a rapid release of heat and necessitates promote evacuation of the product from the reaction vessel; this operation leads to sudden rise of the styrene concentrations in the workplace atmosphere, and the workers involved are exposed to the danger of severe intoxication with sequelae such as encephalopathy and toxic hepatitis unless they are protected by suitable respirators.

Leakages, the need for maintenance workers to enter reaction vessels for cleaning, manual sampling through openings in vessels, may result in exposure to high concentrations of styrene.

Chronic Poisoning

The styrene may also cause chronic poisoning. Prolonged exposure to styrene vapours in concentrations above the TLV [50 ppm (213 mg/m^3)] may result in functional disorders of the central nervous system, irritation of the upper respiratory airways, haematological changes (in particular leukopenia and lymphocytosis) and also in hepatic and biliary tract conditions.

Medical examination of workers employed for over 5 years in polystyrene and synthetic rubber plants, in which the atmospheric styrene and ethylbenzene concentrations were around 50 mg/m^3, revealed cases of toxic hepatitis. Prolonged exposure to styrene concentrations of less than 50 mg/m^3 caused disorders of certain liver functions (protein, pigment and glycogen). Polystyrene production workers have also been found to suffer from asthenia and nasal mucosa disorders; ovulation and menstruation disorders have also been observed.

Experimental research in rats have revealed that styrene exerts embryotoxic effects at concentrations of 1.5 mg/m^3; its metabolic styrene oxide is mutagenic and reacts with microsomes, proteins and nucleic acid of the liver cells. Styrene oxide is chemically active and several times more toxic for rats than styrene itself.

SAFETY & HEALTH MEASURES

- Atmospheric contamination of styrene during the handling or use should be minimised.
- Plant and equipment should be designed and laid out in accordance with modern criteria of technology, safety and health.
- Waste-gas outlets from ovens and furnaces should carry the gases to the open air.
- Continuous process should be given preference over batch techniques.
- Manual operations should be mechanised, and wide use should be made of automation and remote control.
- Ducting, piping and pipe joints should be leak-tight.
- Glandless pumps and measuring and control instruments should be used more widely.
- The atmospheric concentrations of styrene at the workplace should be monitored continuously.
- General and local ventilation should be provided at workplaces and supplemented by exhaust hoods over vapour emission sources and at leaks of sampling points.
- Minimise the level of residual styrene monomer in polystyrene, synthetic rubber and latex to reduce the release of styrene monomer in the air and its harmful effects.
- Spray-painting or product cleaning vapours should be enclosed and fitted with exhaust ventilation, air curtains, special dryers, etc.
- Before workers are allowed to enter a reaction vessel for cleaning purposes, the vessel should be emptied, cleaned from residues, purged and well ventilated.
- Personal Protective Equipment such as hand gloves, goggles, overalls, chemical cartridge or airline respirators, etc., should be supplied to workers who may be exposed to high concentration of styrene.
- Workers entering vessels in which the atmosphere may be severely contaminated with styrene should wear suitable airline respirator.

- Workers who are to be employed on work entailing prolonged exposure to styrene should receive pre-employment and periodical medical examinations.
- Pre-employment examinations should include in particular those persons with liver, kidney, nervous-system, blood and haemopoietic-organ disorders, who are exposed to styrene.
- Persons found to have symptoms caused by action of styrene should be temporarily or permanently be removed from exposure, depending upon the degree of poisoning.
- Carry out periodical Safety Audit of the plant.
- Carry out a Hazard Identification and Risk Assessment study of the plant.
- Maintain Material Safety Data Sheets (MSDS) for all the chemicals used in the plant and circulate the same to the employees.
- Store styrene as per the chemical norms and follow the safety rules strictly.
- Provide Health and Safety training to the operators, supervisors and managers who are involved in the production activities.
- Prepare an On-Site Emergency Plan for the plant and carry out Mock Drills.
- Participate in the preparation of Off-Site Emergency Plan by the statutory authorities.
- Conduct Evacuation Drills periodically.
- All maintenance operations should be done strictly as per Standard Operating Procedures (SOPs)

INDIAN REGULATIONS

According to The *Manufacture, Storage and Import of Hazardous Chemicals Rules, 1989*, framed under the *Environment (Protection) Act, 1986*, styrene is classified as a toxic and hazardous chemical under Schedule 1, Part II. The Rule 128 prescribed under section 112 of the *Factories Act, 1948*, gives, the Permissible levels of certain chemical substances in work environment and wherein the styrene is included. The other related acts/regulations are:

- *Chemical Accidents (Emergency, Planning, Preparedness and Response) Rules, 1996.*
- *Hazardous Waste (Management Handling and Transboundary Movement) Rules, 1989.*
- *Environment (Protection) Rules, 1986.*
- *Public Liability Insurance Act, 1991.*

CONCLUSION

The styrene gas was leaked from *Visakhapatnam* plant of *LG Polymers India Private Limited* on the wee hours of 7th May, 2020. The gas leak killed 12 persons and injury to over 300 persons out of which 20 were in ventilators. The gas leak could have occurred due to polymerisation inside the storage tank. Immediately, after the gas leak, the *Government of India*, has appointed a study team to investigate the accident. The study team submitted its preliminary report on 10th May, 2020 and the details are awaited.

The styrene is a toxic gas and poisoning can happen through inhalation, skin contact, eye contact and ingestion. The initial symptoms can be irritation of the mucous membranes of the upper respiratory tract, the eyes and mouth. These symptoms are followed by nacrosis, cramps and death due to respiratory centre paralysis.

The safety and health measures to be adopted for mitigating the styrene gas leaks are highlighted. All maintenance operations in styrene plant should be carried out as per Standard Operating Procedures (SOPs). Styrene should be stored strictly by observing all safety norms.

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