METHANOL TANK FIRES

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Prepared for Presentation at:

Mary Kay O'Connor Process Safety 2000 Symposium
Beyond Regulatory Compliance,
Making Safety Second Nature

Reed Arena
Texas A&M University
College Station, Texas

October 25, 2000

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Ashland Distribution Company and Ashland Specialty Chemical Company (Ashland) facilities have approximately 68 tanks containing methyl alcohol (methanol) within North America. Three Ashland facilities have experienced tank fires involving bulk storage of methanol during thunderstorms, as noted below:

LOCATION	**TANK SIZE**	**DATE**
Plaquemine, LA	7,000,000 gallons	June, 1989
Tampa, FL	450,000 gallons	July, 1995
Savannah, GA	30,000 gallons	August, 1996

Each storage tank was aboveground and vertical with a weak-seamed, fixed (cone) roof. These tanks sustained damage and could not be salvaged. A special team was assembled after the Savannah fire to investigate and propose recommendations for preventing a recurrence. It determined that lightning and the combination of the following four conditions resulted in ignition with subsequent fire and tank damage:

1. Physical properties of methanol;
2. Weather conditions;
3. Low tank inventories; and
4. Tank venting design.

Methanol Properties

It is believed that methanol is more susceptible to ignition and fire from seasonal lightning strikes than other flammable liquids due to the following unique combinations of physical properties:

- *Widest flammability range of Ashland solvents*
  (6.0 to 36.5% - flammable between 45 and 110^{o} F)

- *Middle of vapor flammability range at 87^{o} F*
  (Minimum ignition energy requirements)

- *Low flash point*
  (54^{o} F)

- *High molecular oxygen content*
  (50%)

- *High vapor pressure*
  (45-277 mm Hg flammable range; significant tank venting in the summer)

- *Low vapor density*
  (1.1 relative to air; vapors will accumulate over/around the tank)

- *Highly polar solvent with water affinity*
  (Methanol can form a conductive electrical path)

- *Minimum Oxygen Content (MOC) for combustion is lower*
  (10% - calculations indicate oxygen levels were well above the MOC levels in tanks at time of ignitions)

Ashland's other flammable liquids have some, but not all, of these properties. Many solvents have high vapor densities and sink to the ground when vented from a tank that is breathing. Many solvents are too rich inside the tanks at summer temperatures to support combustion. For example, an aboveground vertical storage tank with a cone roof containing methyl ethyl ketone (MEK) was struck by lightning in Cincinnati, Ohio creating a hole in the tank, but no ignition. The MEK was probably too rich to burn since vapor concentrations are above the upper explosive limit (UEL) at temperatures greater than 70^{o} F. A comparison of methanol properties to a few selected solvents is shown below:

SOLVENT	VAPOR DENSITY	FLAMMABLE RANGE	VAPOR PRESSURE
Methanol	1.1	6.0 to 36.5% (45-110^{o} F)	160 mm Hg @ 87^{o} F (mid point of flammable range)
Toluene	3.1	1.3 to 7.0% (45-95^{o} F)	30 mm Hg @ 80^{o} F (mid point of flammable range)
MEK	2.4	1.8 to 10.0%	Too rich to burn at temperatures exceeding 70^{o} F
Hexane	3.0	1.2 to 7.5%	Too rich to burn at temperatures exceeding 50^{o} F
Acetone	2.0	2.6 to 12.8%	Too rich to burn at temperatures exceeding 45^{o} F

It is interesting to note the comparison to toluene, for which there are a number of case histories of ignitions and fires/explosions. Like methanol, toluene is near the middle of its flammable range at typical summer temperatures; however, toluene has a much lower vapor pressure than methanol and a much higher vapor density. In addition, toluene is non-conductive, which causes it to be at more risk from static ignitions.

Weather Conditions

Weather conditions during the incidents were considered to be favorable for an ignition and fire. Meteorological data before and during the Savannah incident was analyzed. Air temperature, humidity, wind and rain patterns appeared to be optimal for an ignition and fire. It is believed that weather conditions during the previous two incidents were similar based on the time of day, time of year and comments made by facility personnel.

Tank Inventories

Each methanol tank had significant vapor spaces at the time of the fires. The Tampa tank was 90% empty, the Savannah tank was 75% empty and the Plaquemine tank was 50% empty. The burning methanol vapors rapidly pressurized the tanks due to the large vapor spaces and the weak-seamed cone roofs detached from the shell as designed to relieve the pressure.

Tank Venting Design

All tank venting was installed pursuant to applicable codes. However, the codes do not require that tanks be designed and operated to prevent flammable vapor mixtures from existing inside or forming outside of the tanks. Flammable methanol vapors inside the tanks vented through roof mounted conservation vents on the tanks in Savannah and Tampa, while the tank in Plaquemine vented through a water scrubber. The presence of flammable vapors inside and outside the tanks provided a conductive path for tank vapor space ignition by lightning.

INVESTIGATION FINDINGS

Incident Information

The following were common conditions for the three fires:

- Tanks were located in the southeast;
- Fires occurred during summer afternoon thunderstorms;
- Lightning strikes were attributed as the cause of the fires based on facility personnel observations;
- Tanks were vertical (35-40 ft tall), weak-seamed, cone roof design;
- Roofs released from the shells after ignition and pressurization (as designed);
- Tank grounding was intact after the incidents (Savannah inspection noted no evidence of overheating);
- Tanks had significant vapor spaces at time of incidents; and
- No transfers were being done prior to the fires.

There was no activity with the Savannah and Tampa tanks the day of the fires and all tank valves were closed. The Savannah storage tank had a 2-inch conservation vent and a 6-inch emergency vent, while the Tampa storage tank had a 2-inch conservation vent and an 8-inch emergency vent. These tanks were not provided with any flame arrestors. At Savannah, the flammable storage tanks (including toluene) next to the methanol tank were full.

The Plaquemine storage tank shared a vent line to a water scrubber with another large methanol storage tank. The vent line between the tanks was a few hundred feet long. A flame arrestor was installed on the Plaquemine tank vent according to incident file notes, but the location on the vent line is not known. It is not known if there were conservation vents on these two tanks.

Industry Tank Fire Information

No other documented or reported incidents of methanol tank fires from lightning strikes were found. The investigation team came to this conclusion after discussions with the following sources:

- American Petroleum Institute (API);
- American Methanol Institute (AMI);
- Lightning Protection Institute (LPI);
- Residuals Management Technology (RMT);
- United Service Agency (USA); and
- Various methanol producers and handlers.

The investigation team is not aware of any mechanism for companies to use to report fires. However, API contracted Loss Control Associates to conduct and publish a survey of large diameter tank fires in 1996. The survey covered a time frame from 1951 through 1994. There were no reported incidents of methanol tank fires, although many of the reported fires did not list tank contents.

According to the API survey, there was an average of about 10 large tank fires per year from 1990 through 1994. The predominant cause was lightning (over 50%). In most of the case histories presented, it was not known whether a direct or indirect stroke of lightning had caused the ignition.

Industry Practices and Recommendations

<u>There is no recognized methanol industry consensus standard for prevention of fires in methanol storage tanks</u> based on literature reviews and discussions with methanol producers, terminal operators and industry trade associations. Methanol industry practices vary and include floating roof tanks, inert gas blanketing, flame arrestors and tank grounding. Floating roof designs have also been installed for emission controls and possibly for improved quality.

The investigation team attempted to identify and contact all methanol producers and large terminal operators in the southeast. To our knowledge, these producers and operators have either floating roof or nitrogen blanketed tanks at this time (one producer recently retrofitted their tanks with floating roofs). A survey of a few producers outside of the southeast indicated that some had nitrogen blankets, while others did not have a floating roof or nitrogen blanket. However, they did have flame arrestors and tank grounding as specified in *NFPA 780, Lightning Protection Systems.* The investigation team did not contact any end users of Ashland methanol.

The API document 2021A, *Interim Study – Prevention and Suppression of Fires in Large Aboveground Atmospheric Storage Tanks* was published in July of 1998. This publication provides the user with information needed to make decisions concerning fire prevention and protection. It also offers guidelines on preventative measures that can be used to reduce the risk of occurrence of tank fires. One referenced measure is the use of floating roof tanks for flammable liquids with a vapor pressure greater than 1.5 psia (78mm Hg). Methanol has a vapor pressure of 3 psia (156mm Hg) at 85^{o} F. Another referenced measure is the use of inert gas blanketing.

The Aboveground Storage Tank Guide published in August of 1996 by the Thompson Publishing Group states that, "Mounting evidence indicates that additional...precautions and preventative maintenance may be the key to reducing the number of AST (Aboveground Storage Tank) fires caused by lightning strikes." Floating roof tank installation was referenced as one possible precaution.

Code and Standard Requirements

There are no specific regulatory requirements for fire prevention controls on methanol tanks. With respect to venting, *NFPA 30, Flammable and Combustible Liquids Code*, and *API 2000, Venting Atmospheric and Low-Pressure Storage Tanks: Nonrefrigerated and Refrigerated*, require either a normally closed vent (conservation vent) or a flame arrestor device in an open vent for flammable liquid storage. This is Ashland's standard practice for flammable liquid storage installations.

The NFPA 780 standard states that cone roof metallic tanks are considered to be inherently self-protected against lightning if the following requirements are met:

- All joints between metal plates are riveted, bolted or welded;
- All pipes entering the tank are metallically connected to the tank at the point of entrance;
- All vapor or gas openings are closed or provided with a flame protection device (self-closing gauge hatches, vapor seals, pressure-vacuum breather vents or flame arrestors);
- Roof has a minimum thickness of 3/16 inch; and
- Roof is welded, bolted or riveted to the shell.

API Recommended Practice (RP) 2003, *Protection Against Ignitions Arising out of Static, Lightning, and Stray Currents*, states that metallic cone roof tanks maintained in good condition are well protected from ignition or damage by direct-stroke lightning. RP 2003 notes that explosions caused by lightning have occurred in oil tanks where roof openings were left open or vents were not protected by backflash devices. RP 2003 further states that pressure-vacuum vents are known to prevent propagation of flame into a tank if escaping vapor ignites.

Electrical Lightning Protection Systems

Application of electrical lightning protection systems beyond conventional tank grounding was investigated. It was determined that this course of action would not effectively reduce risk at Ashland facilities. Methanol producers and handlers contacted said they had no special lightning protection systems in place at their tanks.

Lightning protection system standards and guidelines from the American Petroleum Institute (API), the National Fire Protection Association (NFPA), and the Industrial Risk Insurers (IRI) were reviewed. The Lightning Protection Institute and United Service Agency were also contacted.

The API and NFPA standards on lightning protection systems state that metallic tanks and structures that are properly built, sealed, vented and grounded are inherently self-protected and have proven to be adequate for safe dissipation of lightning strokes. The API and NFPA only reference consideration of lightning rods, conducting masts or overhead wire protection systems for structures made of insulating materials such as wood, brick, tile or concrete.

<u>LIGHTNING IGNITION THEORIES</u>

Tank Venting Scenario

The following proposed sequence of events for the Savannah incident is based on an analysis of meteorological data from the National Weather Service station for Savannah (US Department of Commerce, National Oceanic and Atmospheric Administration). It is presumed that this scenario is similar for the Tampa and Plaquemine incidents based on the times of day, times of year and comments from facility personnel.

1. The methanol tank heated and vented during the morning hours, which caused temperatures to increase from 73 to 85^{o} F (optimal temperature for methanol ignition). Calculations verified that vapor would be vented due to the warming, ambient temperatures.

2. Methanol vapors accumulated over the top of the tank during the dead calm before the afternoon storm.

3. Some time before ignition, winds started to mix air with the methanol vapors and partially dispersed the mixture. Relative humidity was 90-100% which, combined with the methanol vapors, would have created a very conductive path in the air around the tank.

4. During the few minutes prior to ignition, ambient temperatures dropped from 85 to 73^{o} F. Rain started prior to ignition, which could have accelerated the

temperature drop inside the tank and caused more in-breathing through the vacuum vent.

5. Lightning then struck at or near the tank and vapors ignited outside the tank. Fire propagated into the tank through the open vacuum vent.

6. The tank pressurized rapidly due to large vapor space, causing the weak-seamed cone roof to disengage from the shell as designed to relieve pressure. The facility personnel reported that the loud sound from the roof separation occurred within seconds of the observed lightning strike(s).

Cause of Ignition

It is not clear whether the ignition occurred from a direct or indirect lightning stroke. There were no documented reports of damage to the tanks or vent hardware that could be conclusively attributed to a direct hit. The 2-inch vent on the Savannah tank sustained internal damage in the form of a bent pressure poppet stem and a damaged weight. In addition, some burn marks were initially observed on the inside surface of the 2-inch vacuum poppet disc, but were no longer visible during later inspections in Columbus.

API RP 2003 on lightning protection describes indirect lightning phenomenon as "...sparks or corona (which) can discharge to the atmosphere at elevated points on the equipment or between separate conductive objects that are in the path of a lightning-caused current." Electrical engineers were consulted and confirmed that these sparks or coronas could travel some distance.

The following ignition theory has been postulated:

> Methanol vapor above or near the tank combined with water vapor from high humidity to provide a conductive path for a stray lightning-induced current (corona) to travel to the grounded tank. Ignition occurred when the stray current reached a flammable mixture at or near the tank vent. The wide flammability range of methanol, low vapor density and optimal climatic conditions suggest that a zone of flammable vapors could have existed at some distance outside the tank prior to ignition.

Point of Ignition

There are two suppositions regarding the possible point of ignition.

The first supposition is that ignition occurred outside the tank and propagated into the tank through the conservation vent. This follows the more conventional belief or theory on how tanks containing flammable liquids could catch on fire. A flame arrestor installed upstream of the conservation vent could prevent this tank ignition scenario.

<u>The second supposition</u> is that an arc occurred across the vent and ignition occurred inside the vent or just inside the tank's vapor space. This proposal is considered to be plausible based on electrical theory analysis due to the conductivity of methanol vapors inside and outside the tank. If a stray current were attracted to a spot on the tank roof near the vent, then an arc could occur across the vent as the current discharged through the tank to ground. The internal ignition supposition was described as the most predominant theory behind the cause of the Plaquemine fire. A flame arrestor may not prevent this tank ignition scenario, although proper bonding and grounding should minimize the probability by providing a path of least resistance to discharge the current.

<u>RISK ASSESSMENT</u>

Methanol storage tanks in the southeast United States are considered to be at higher risk for fires from lightning strokes due to their locations. The factual and theoretical rationales for this risk determination are described below.

Factual Rationales

Tanks are located in an area of the country with the highest frequency of thunderstorms. Figure H-2(a) in NFPA 780 illustrates mean annual days with thunderstorms on a plot of the contiguous U.S. based on the period 1948-1972. The highest frequency is between the Orlando and Tampa area at 130 days per year. Savannah and Plaquemine average 80 and 90 days per year, respectively. Columbus, Ohio (by comparison) averages 60 days per year. Other parts of the country range between 5 and 50 days per year.

The only known methanol fires from lightning have occurred at the Ashland facilities in the southeast.

All methanol producers and terminal operators contacted in the southeast have floating roofs or inert gas blankets.

There are some producers with tanks located outside the southeast that do not have floating roofs or nitrogen blankets.

Theoretical Rationales

Favorable weather patterns exist in the southeast.

> Thunderstorms in this area often move through during summer afternoons when climatic and tank venting conditions can be favorable for an ignition and fire.

Types of thunderstorms in the southeast.

> Southeast summer storms are influenced by the Gulf of Mexico and are characterized by rapidly developing and violent weather fronts that occur almost daily. These conditions are much less pronounced in geographical areas outside

the designated higher risk southeast corridor. As a comparison, typical thunderstorms in the Ohio Valley develop slowly during the day and sometimes last into the night.

CONCLUSION

Lightning appears to have a natural attraction for storage tanks containing bulk methanol, principally due to its physical properties. The probability for fire increases based on storage practices and geographic location. Currently, there is no industry-wide fire prevention standard for methanol storage tanks. It is recommended that methanol be stored in a floating-roof tank or under an inert gas blanket, with a flame arrestor upstream of the conservation vent as well as tank bonding and grounding. A rigid preventative maintenance program including electrical continuity measurement must be in place for these systems to ensure their integrity.

REFERENCES

API Std 2000 – *Venting Atmospheric and Low-Pressure Storage Tanks: Nonrefrigerated and Refrigerated*, 5th Edition, April 1998.

API RP 2003 – *Protection Against Ignitions Arising Out of Static, Lightning and Stray Currents*, 6th Edition, September 1998.

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EPA 550-F-97-002c – *Lightning Hazard to Facilities Handling Flammable Substances*, May 1997.

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INVESTIGATION PERSONNEL

The author would like to acknowledge the following individuals for their support and participation in this project:

Ashland Distribution Company
Dan Dugan
Mark Vagasky
Russ Walters
Buddy Whitlock

Ashland Inc. Environmental Health and Safety
Joel Howard
Jim Mobberly
Eric Roberts

Ashland Specialty Chemical Engineering
Ed Franz
Jerry Jackson
Larry Krick
John Mansperger
John Raymond
Lou Schaumleffel
Jay Schnaith

Ashland Specialty Chemical Petrochemical Division
Keith Clark
Richard Demboski
Mike Lewis
Paul Moschell
Ed Steinmetz

Pro-Tech-Safety
Jim Mills

Residuals Management Technology
Dr. Sam Mannan
Wamac Soward

United Service Agency
Dave Allen
Bob Henley