Vapor Cloud Explosions and Fires

All of us are aware of vapor cloud or gas explosions and fire and the resulting damage that occurs. Many occur at industrial complexes which handle fuels or manufacture chemicals. They can also occur at Liquefied Natural Gas (LNG) Plants, for example, the LNG production plant at Skikda, Algeria, on 19 January 2004. Residential areas are not immune to explosions resulting from ignition of natural gas leaks. Transportation accidents may result in the release of fuels.

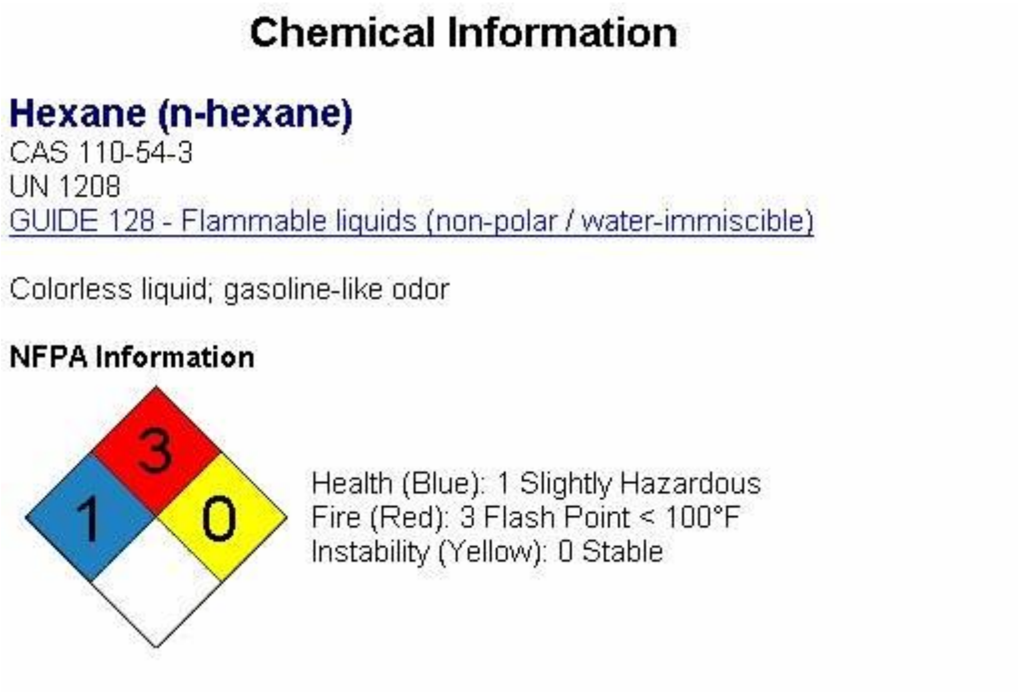
Before the 11 September 2001 attacks on the World Trade Center and the Pentagon, no one seriously considered that terrorists would use commercial aircraft carrying a full load of fuel to destroy targets on the ground.

The difference between a gas explosion and vapor cloud explosion has to do whether the material is a gas or liquid at ordinary temperatures and pressures. Methane and propane would be considered as a gas but fuels such as gasoline, hexane, and cyclohexane are liquids which can vaporize forming a vapor cloud. Finely divided combustible solids dispersed in the air as in a grain or corn silo can also ignite resulting in a serious explosion.

The term, “Unconfined Vapor Cloud Explosion” apparently was coined following the 1 June 1974 accident at a chemical plant near Flixborough, UK. This accident involved the rupture in a 20-inch bypass pipe dumping almost 40 tons of cyclohexane which vaporized. The resulting vapor cloud found an ignition source; the blast and fire destroyed the entire chemical complex killing many people. The word “unconfined” can be misleading. While the cyclohexane vapor was outdoors as opposed to being inside a tank or pipe, the chemical equipment, ground surface, and buildings provided some confinement which influenced the blast overpressure and damage.

Analysis of vapor cloud explosions at industrial facilities can be complex. For example, the U.S. Chemical and Hazard Investigation Board investigated the 23 March 2005 explosions and fire at BP’s Texas City refinery which killed 15 people and injured 170 others. The CSB investigative team interviewed over 350 witnesses, collected tens of thousands of documents, and expended about $2 million dollars to conduct the investigation. An impressive animated video of the accident and causes can be viewed at the CSB website, at http://www.csb.gov/index.cfm?folder=current_investigations&page=info&INV_ID=52#launch [click on: “ CSB Animation of BP Texas Refinery Accident” video produced 27 Oct. 2005.]

Before we continue further with vapor cloud and gas explosions, let’s look at some definitions. We might consider as an example the chemical hexane. The display in the PEAC tool for hexane under physical properties is illustrated below:



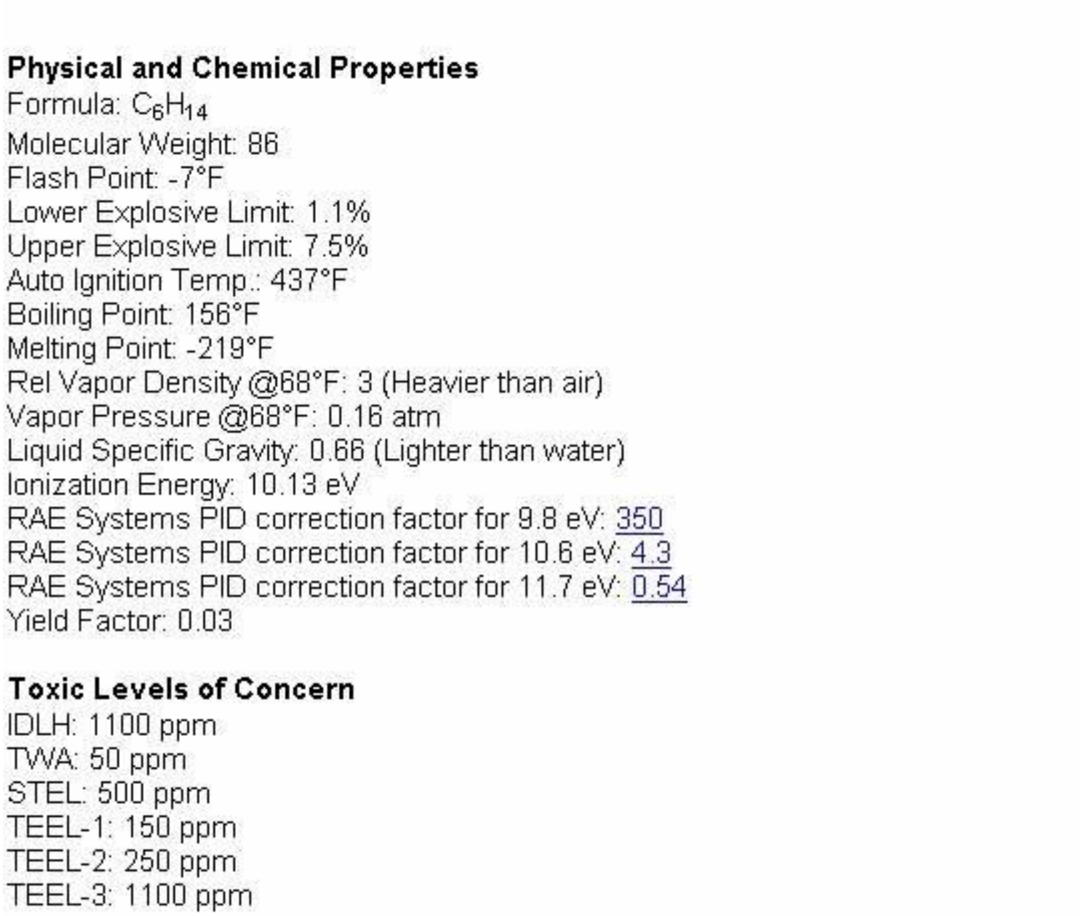
Chemical Information

Hexane (n-hexane)
CAS 110-54-3
UN 1208
GUIDE 128 - Flammable liquids (non-polar / water-immiscible)

Colorless liquid; gasoline-like odor

NFPA Information

Health (Blue): 1 Slightly Hazardous
Fire (Red): 3 Flash Point < 100°F
Instability (Yellow): 0 Stable



Physical and Chemical Properties
Formula: C_6H_{14}
Molecular Weight: 86
Flash Point: -7°F
Lower Explosive Limit: 1.1%
Upper Explosive Limit: 7.5%
Auto Ignition Temp.: 437°F
Boiling Point: 156°F
Melting Point: -219°F
Rel Vapor Density @68°F: 3 (Heavier than air)
Vapor Pressure @68°F: 0.16 atm
Liquid Specific Gravity: 0.66 (Lighter than water)
Ionization Energy: 10.13 eV
RAE Systems PID correction factor for 9.8 eV: 350
RAE Systems PID correction factor for 10.6 eV: 4.3
RAE Systems PID correction factor for 11.7 eV: 0.54
Yield Factor: 0.03

Toxic Levels of Concern
IDLH: 1100 ppm
TWA: 50 ppm
STEL: 500 ppm
TEEL-1: 150 ppm
TEEL-2: 250 ppm
TEEL-3: 1100 ppm

Figure 1 – PEAC-WMD Chemical Information for n-Hexane

Comment: The PEAC tool also displays information using metric units.

Definitions

- **Auto Ignition Temperature**: This is the temperature above which spontaneous combustion can occur without an ignition source (spark or flame). While many data bases including the PEAC tool lists auto ignition temperatures for particular chemicals, the actual auto ignition temperature is also dependent upon the concentration of chemical in the air and the material that it is in contact. For example, according to the National Fire Protection Association (NFPA), the auto ignition temperature of benzene measured in an iron flask is almost 200^{o}F higher than when measured in a quartz flask. The auto ignition temperature of 1.5% pentane in air is 129^{o}F higher than that for a 7.65% concentration in air.

- **Flash Point:** This is the lowest temperature at which a flammable liquid exposed to air will burn when exposed to sparks or flame. The flash point is determined from laboratory tests. Several laboratory tests are available: (1) closed cup tag, ASTM procedure D-65, used for materials of 194^{o}F (90^{o}C) flash point or less; (2) Pensky Martens, (ASTM procedure D-93), used for materials of 194^{o}F (90^{o}C) or greater flash point; (3) Open cup tag (ASTM procedure D-1310); and Cleveland test (ASTM procedure D-92). Many listings such as the NIOSH pocket guide do not list flash points for flammable gases; if a flashpoint is listed for a gas in a data source the chemical is assumed to be liquefied.

- **Flammable Limits:** The flammable limit is the range of composition of material in air which will burn. The Upper Flammable Limit (UFL) is the highest volume percent composition in air in which the material will burn. The Lower Flammable Limit is the lowest volume percent composition in air in which the material will burn.

- **Explosive Limits:** Same as flammable limits.

- **Vapor Pressure:** Pressure exerted by liquid (or solid) on the vapor space. For example, the vapor pressure for hexane at 68^{o}F (20^{o}) is 0.16 atm. At sea level elevation, the total atmospheric pressure is 1 atmosphere which means that if some hexane is placed in a container and the container is allowed to vent to the air the volume percent concentration of hexane in the air space above the liquid will reach 16% at 68^{o}F. The vapor pressure increases with increasing temperature. At the boiling point of hexane (156^{o}F), the vapor pressure will be 1 atmosphere. At a high elevation location where the total atmospheric pressure is say 0.75 atm the vapor pressure of hexane is still 0.16 atm at 68^{o}F (20^{o}C), but now the volume percent vapor in a vented container is now (0.16/0.75) x 100% = 21.3%.

- **Reid Vapor Pressure:** Vapor pressure measured at 100^{o}F (37.8^{o}C). The vapor pressure of hexane at 100^{o}C is 0.34 atm or 5 psi. The Reid vapor pressure is used in the petroleum refining industry especially in the specification of fuel blends.

- **Flammable Liquid:** The NFPA defines a flammable liquid as a liquid with a flash point less than 100^{o}F (38^{o}C).

- **Combustible Liquid:** The NFPA defines a combustible liquid as a liquid with a flash point greater than or equal to 100^{o}F (38^{o}C).

- **Light end hydrocarbons:** The petroleum industry defines light end hydrocarbons as liquids which vaporize when exposed to air, in particular, hydrocarbons with a Reid vapor pressure greater than 15 pounds per square inch absolute (psia). Examples are pentanes and lighter napthas.

- **High Flash Stocks:** The petroleum industry defines high flash stocks as liquids with a flash point greater than or equal to 130^{o}F (55^{o}C) or stored at temperatures of at least 15^{o}F (8^{o}C) below its flash point. An example is heavy fuel oil.

- **Low Flash Stocks:** The petroleum industry defines low flash stocks as liquids with a flash point less than 130^{o}F (55^{o}C) or stored at temperatures within 15^{o}F (8^{o}C) below its flash point. An example is Diesel fuel.

- **Ignition Source:** Fire or flames, electrical sparks, or even very hot surfaces may serve as ignition sources. The fire may come from a furnace, flares, welding, sparks from tools, matches and lighters, or cigarettes. Electrical sparks may originate from switches and motors, electrical equipment lightning, or buildup of static electricity. A 1959 fire at the University of Minnesota Chemistry building was caused by someone transferring a flammable liquid (benzene) from an ungrounded 55 gallon drum to smaller containers for use in a laboratory; the pouring of the liquid caused a buildup of static charge which sparked igniting the liquid. Hot surfaces near or above the auto ignition temperature (e.g. hot pipes, equipment, vehicle equipment) may cause fuel to ignite even without spark or flame.

- **Deflagration:** Propagating reactions in which the energy transfer from the reaction zone to the unreacted zone is accomplished thru ordinary transport processes such as heat and mass transfer. An example is fire, although the term deflagration is usually used for a fire that burns fast (combustion processes with flame speeds on the order of 0.5 to 1 meter/second).

- **Detonation:** Propagating reactions in which energy is transferred from the reaction zone to the unreacted zone on a reactive shock wave. The velocity of the shock wave always exceeds sonic velocity in the reactant. This is the blast or explosion.

- **Explosion:** Explosions result when combustion occurs so rapidly that there is a large buildup of pressure from the combustion by-products resulting in a shockwave. The shockwave expanding is the explosion (detonation). If combustion is not that rapid we get deflagration (a fire).

<u>Questions for Discussion</u>

1. A sniper using a high powered rifle fires at a tanker truck carrying gasoline (petrol). Would there be a fire or explosion if the bullet penetrates the tank?

Answer: Unlikely, unless the gasoline leaks out from the tank and is ignited outside the tank. Liquid gasoline does not burn; it is gasoline vapor in contact with air oxygen which burns or could explode. The concentration of gasoline vapor in air must be between the lower explosive limit and upper explosive limit for gasoline. The PEAC tool lists the lower explosive limit as 1.4% and the upper explosive limit as 7.6%. These numbers might vary somewhat depending how the gasoline was formulated (another reference source lists 7% as the upper explosive limit). At 68^{o}F (20^{o}C) the vapor pressure for gasoline is 0.39 atm, which translates to 39% vapor concentration by volume. The Reid Vapor Pressure of gasoline [recall that this is the vapor pressure at 100^{o}F] is about 9.5 psi, or 0.647 atm, which converts to 64.7% vapor concentration by volume. These are above the upper explosive limit, and therefore, the gasoline does not ignite.

1. Are there circumstances where the gasoline inside the tanker truck can ignite and explode?

Answer: Yes. If the tanker truck is essentially empty, the vapor concentration in the tank can drop below 7.6% and ignite and explode if there is an ignition source. This is why welding of gasoline tanks are especially dangerous; the tank must be purged with an inert gas. Interestingly, the vapor space in a partially filled tanker truck could become flammable under very cold temperatures (between 0^{o}F or 10^{o}F and -45^{o}F for gasoline). The flash point for gasoline is -45^{o}F (some references say -40^{o}F). At 5^{o}F, the vapor pressure is about 0.076 atm or 7.6% (the numbers may vary depending upon the gasoline formulation).

1. If gasoline (petrol) spills on a hot surface such as an automobile exhaust system, will it ignite?

Answer. Probably not, as the auto ignition temperature of gasoline (from the PEAC tool) is 853^{o}F (456^{o}C). Exhaust systems are not that hot. As pointed out in the definitions, there are a number of variables that affect the auto ignition temperature so any hot surfaces that even near the auto ignition temperature of a fuel have the potential to ignite the fuel. Of course, a spark can ignite the fuel.

1. Does the same situation hold for diesel fuel?

Answer: Not quite; the flash point, auto ignition temperature, vapor pressures, lower and upper explosive limits are different. The flash point for diesel fuel is between 70^{o}F and 140^{o}F depending upon the formulation [typically 120^{o}F or 49^{o}C], which makes diesel fuel difficult to ignite if a bullet is fired into a diesel fuel tanker. The auto ignition temperature of diesel fuel is considerable less than gasoline (one reference lists 351^{o}F or 177^{o}C) making it somewhat easier to ignite when contacted with a very hot surface. The vapor pressure of diesel fuel is much less than gasoline; under normal temperatures, the vapor pressure in a tanker truck should result in a vapor concentration less than the lower explosive limit. Upper and lower explosive limits are different for different formulations [e.g. LEL: 0.4 to 6%; UEL: 8% to 13.5%].

1. Why is the combination ammonium nitrate-fuel oil (ANFO) an explosive combination?

- *Answer:* The nitrate supplies the oxygen for the reaction and the fuel oil supplies the fuel. Air oxygen is not required. When ammonium nitrate and fuel oil is mixed in the right proportions the reaction is so rapid that there is a large buildup of pressure from the combustion by-products (ammonia, nitrogen, carbon dioxide, etc.) resulting in a shockwave. A combination which results in maximum explosive effect is blasting grade ammonium nitrate prills soaked in fuel oil (94% ammonium nitrate, 6% fuel oil) and detonated by a high explosive booster or blasting cap. The shockwave expanding what produces the explosion. The material detonates.

1. If there is a hypothetical cloud of propane up in the air away from the ground or anything that might confine the propane, and the cloud contacts an ignition source, will it detonate or deflagrate?

Answer: Deflagration is the better answer. [left photo, propane deflagration, from Baker Engineering & Risk Engineering Inc. website]. We will assume that the cloud concentration is between the lower and upper explosive limits, although the concentrations at the edge of the cloud may tail off below the lower explosive limit. The combustion front will be very rapid but will probably not reach sonic velocities. With nothing to restrain the front (e.g. ground, structures, a tank), the large overpressures associated with a blast may not occur. The result will be a huge fire ball. The same is true for methane. There would be catastrophic fire damage but relatively low explosion potential. There is some debate in the literature on how much blast damage would occur.

1. What are the conditions that result in vapor cloud explosions as opposed to a deflagration?

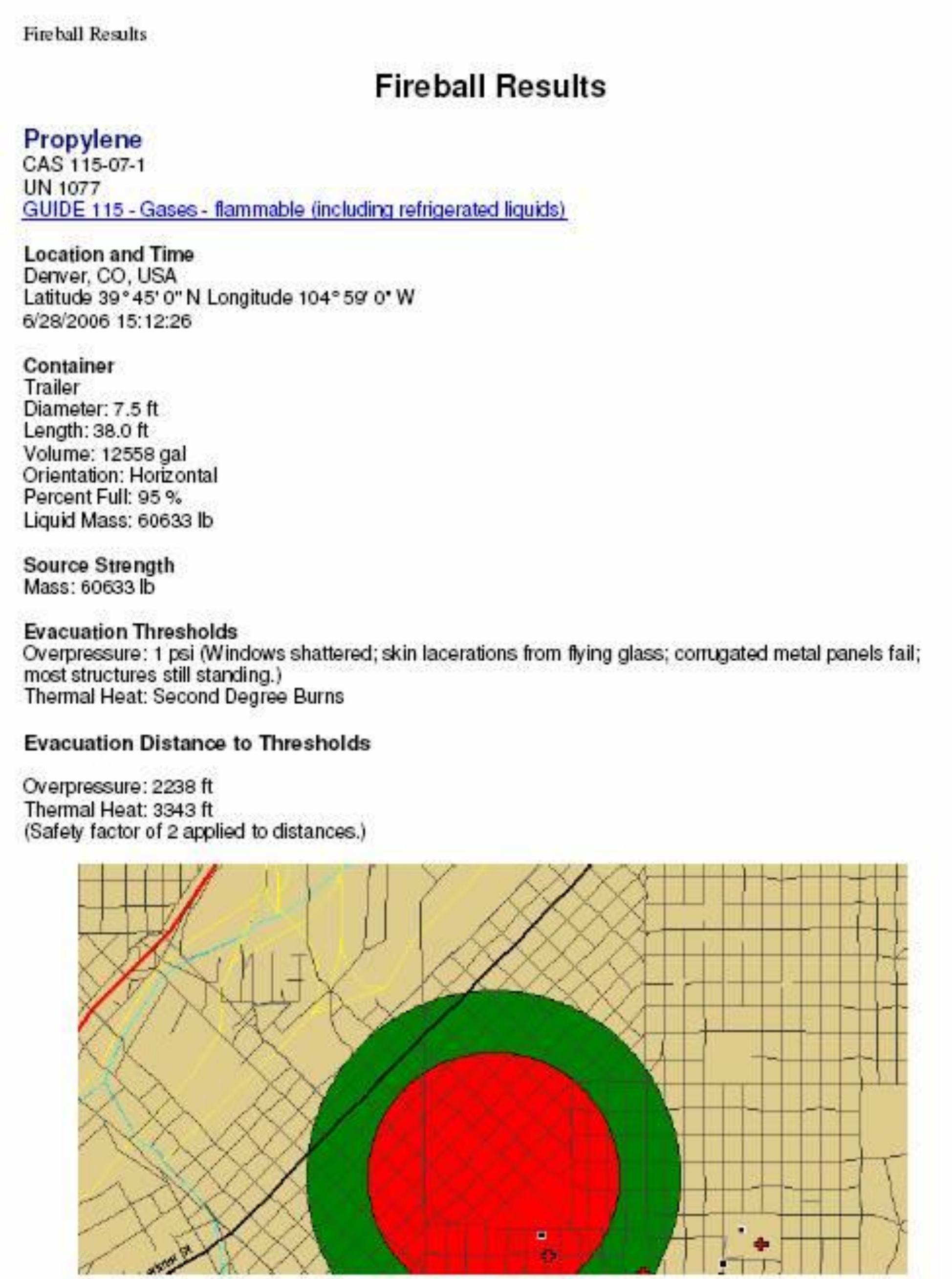
Answer: This is a complex issue which is not easily answered. The vapor cloud concentration must be between the lower and upper explosive limit. The material itself is a factor. Saturated hydrocarbons containing only hydrogen and carbon (e.g. methane, ethane, propane, butane, pentane, hexane, etc. are more to result in deflagration if completely unconfined. Olefins are more likely to detonate (overpressure produced from combustion products). If the fuel is reactive (e.g. acetylene) or contains oxygen (e.g. ethers, ethylene oxide) it is even more likely to detonate. Any nearby structures including the ground which provides a barrier to the combustion front can result in the buildup of overpressures resulting in a blast front.

What is the Basis for the PEAC Tool Calculations?

We will look at an example. Let us select propylene as the chemical. The PEAC tool will then display information about the chemical including flash point, auto ignition temperature, vapor pressure, upper explosive limit, and lower explosive limit. Calculations for a vapor cloud explosion and fireball are initiated by clicking on the fireball icon, which appears at the left.

The PEAC tool first displays a disclaimer statement and then asks the user questions about the amount of propylene released as a vapor cloud. The user can input the mass directly or calculate it based on the original container size or calculate a mass in the container and assume that only part of this forms a vapor cloud. The user can select a blast distance based on either an overpressure or damage profile and a thermal heat distance based on a threshold for second degree burns or 1% fatality or 50% fatality. A partial final display may look like the following:

Some of the details on “Minimum Distances for Blast Overpressure Effects” have been cropped in the display below. Also, two screen images have been merged into one.



Fireball Results

Fireball Results

Propylene
CAS 115-07-1
UN 1077
GUIDE 115 - Gases - flammable (including refrigerated liquids)

Location and Time
Denver, CO, USA
Latitude 39° 45' 0" N Longitude 104° 59' 0" W
6/28/2006 15:12:26

Container
Trailer
Diameter: 7.5 ft
Length: 38.0 ft
Volume: 12558 gal
Orientation: Horizontal
Percent Full: 95 %
Liquid Mass: 60633 lb

Source Strength
Mass: 60633 lb

Evacuation Thresholds
Overpressure: 1 psi (Windows shattered; skin lacerations from flying glass; corrugated metal panels fail; most structures still standing.)
Thermal Heat: Second Degree Burns

Evacuation Distance to Thresholds

Overpressure: 2238 ft
Thermal Heat: 3343 ft
(Safety factor of 2 applied to distances.)

Figure 2 – Fireball Results from the PEAC-WMD application

The PEAC tool follows the methodology used by the U.S. Environmental Protection Agency (EPA) in their Risk Management Assessment in calculation of blast and thermal heat distances as used in 40 CFR Part 68. However, instead of assigning a yield factor of 0.1 for estimating the fraction of the chemical which produces blast energy, the PEAC tool uses the yield factors used by the ARCHIE Model. The EPA uses 0.1 as the yield factor. The yield factors in ARCHIE vary from 0.02 for saturated hydrocarbons to 0.19 for more reactive chemicals.

There are some differences in the literature of some of the details of how to implement these calculations, which means that the ARCHIE model does not exactly give the same answers as say the EPA model even if the same overpressures and yield factors are used. If the explosion occurs in the air well above the ground, the distances are reduced by a factor of 1.26 compared with an explosion at ground level. If the vapor is partly confined as in a building or by walls the blast effects could even be greater. As mentioned before, the PEAC modeling follows the EPA methodology using Yield Factors in ARCHIE.

The citation for EPA is “Risk Management Program Guidance for Offsite Consequence Analysis”, EPA 550-B-99-009, April 1999.

ARCHIE [an acronym for Automated Response for Chemical Hazard Incident Evaluation] was developed under contract with Hazmat America, Inc., in Arlington MA, and by scientists at Arthur D. Little, Inc., for the Federal Emergency Management Agency (FEMA), the U.S. Department of Transportation (DOT), and the U.S. EPA.

There are critics of this methodology who point out that vapor cloud is not a point source but a defuse cloud whose concentrations tail off to essentially zero at the edge of the cloud. The shape of the cloud before ignition is not spherical but is influenced by wind or air movement and by nearby structures. As a rough rule of thumb, the fire will burn at all locations where the vapor cloud concentrations are about half the lower explosive limit or higher; however, ignition takes place between the lower and upper explosive limit values. Therefore, anything between about half the lower explosive limit concentration or higher is expected to be consumed by a fire. The blast waves release energy from the large volume of the ignited vapor cloud and produce blast waves different than from detonation of say TNT or ANFO. Alternative models are (1) TNO Mult-Energy Model, (2) Baker-Strehlow Model, and (3) the Distributed-Source TNT Model. We will not discuss these models here but refer to comparison in a company newsletter published by Quest Consultants, Inc., Norman, Oklahoma, available over the internet at http://www.questconsult.com/, “The Quest Quarterly, Vol 4 No. 1 and Vol 4 No. 2, 1999, specifically http://www.questconsult.com/99-spring.pdf. Another paper, presented by Arthur D. Little staff, discusses the TNT Equivalency method, the TNO Mult-Energy Model, and a computer software calculation package (called AutoReaGas), was presented by H. Ozog and G.A. Melhem at the International Conference and Workshop on Process Safety Management and Inherently Safer Processes, AIChE/CCCP, October 1996, available at http://www.diers.net/iomosaic/pdf/siting.pdf.

The authors H. Ozog and G.A. Melhem, cited above, commented that the peak overpressure within the vapor cloud when ignited probably does not exceed 15 psi above atmospheric. At the edge of the cloud, the overpressure is likely to be 10 psi or somewhat less. Outside the cloud, the overpressure is likely to drop off as a function of distance as predicted by the TNT point source equivalency equation which almost everyone uses including the PEAC tool. At distances far from the cloud where the overpressure is less than 0.5 psi, the overpressure blast wave behaves more like an acoustical wave, and the basic TNT equivalency equation under predicts the distance for a given overpressure.

The authors, J. Jiang, Z.G. Liu, and A.K. Kim presented a paper titled “Comparison of Blast Prediction Models for Vapor Cloud Explosion” sponsored by The Combustion Institute, Canadian Section, 2001 Spring Technical Meeting, 13-16 May 2001 (see http://irc.nrc-cnrc.gc.ca/pubs/fulltext/nrcc44715/). They concluded, “Over the past decades a variety of prediction models have been developed to predict the blast effect at any given distance from a possible explosion source. However, these models have a limited range of applications, and they provide reasonable results only if they are applied correctly within their intended purposes, otherwise they may produce misleading results. Currently, there is no clear recommendation on which model is preferred for a specific case under consideration”

Because of the many uncertainties in modeling vapor cloud explosions and fires, the PEAC tool incorporates a safety factor of two in estimating blast and thermal heat distances.

Aristatek searched the Internet for actual pictures of vapor cloud explosions. There were many pictures available showing the damage occurred or of fires following the explosion but the only pictures available of actual vapor cloud explosions were of specially setup tests such as the photo below rather than of actual industrial facilities. Notice that the explosion image is not hemispherical.

From: http://www.fas.org/man/dod-101/sys/dumb/fae.htm. Military test photo.