



# Flammable Gases And Liquids And Their Hazards



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# **FLAMMABLE GASES AND LIQUIDS AND THEIR HAZARDS**

Office of Pollution Prevention and Toxics  
U.S. Environmental Protection Agency  
Washington, D.C. 20460

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## EXECUTIVE SUMMARY

This report assesses the potential consequences of accidents involving flammable chemicals to support the evaluation of whether such chemicals may warrant addition to the list of extremely hazardous substances (EHSs) under section 302 of Title III of the Superfund Amendments and Reauthorization Act (SARA). EPA's analysis included identification and evaluation of existing listing and classification systems, along with any applicable criteria; review of existing regulations and codes dealing with flammable materials; analysis of histories of accidents involving flammable substances; and modeling potential consequences of fires and explosions of flammable substances.

EPA determined that most classification systems for flammable substances are based on physical/chemical properties, usually flash point and boiling point. The types of flammable substances that are generally classified as most hazardous are flammable gases and volatile flammable liquids, with low flash points and low boiling points. Evaluations of the severity of accidents that could be caused by various flammable substances are not directly considered in the classification systems.

A review of accident history indicates that flammable substances have been involved in many accidents, and, in many cases, fires and explosions of flammable substances have caused deaths and injuries. Accidents involving flammable substances may lead to vapor cloud explosions, vapor cloud fires, boiling liquid expanding vapor explosions (BLEVEs), pool fires, and jet fires, depending on the type of substance involved and the circumstances of the accident.

Vapor cloud explosions produce blast waves that potentially can cause offsite damage and kill or injure people. EPA reviewed the effects of blast wave overpressures to determine the level that has the potential to cause death or injury. High overpressure levels can cause death or injury as a direct result of an explosion; such effects generally occur close to the site of an explosion. EPA's analysis of the literature indicates that people also could be killed or injured because of indirect effects of the blast (e.g., collapse of buildings, flying glass or debris); these effects could occur farther from the site of the blast. A vapor cloud may burn without exploding; the effects of such a vapor cloud fire are limited primarily to the area covered by the burning cloud. The primary hazard of BLEVEs, pool fires, and jet fires is thermal radiation; the potential effects of thermal radiation generally do not extend for as great a distance as those of blast waves. In addition, the effects of thermal radiation are related to duration of exposure; people exposed at some distance from a fire would likely be able to escape. BLEVEs, which generally involve rupture of a container, can cause container fragments to be thrown substantial distances; such fragments have the potential to cause damage and injury. Fragments and debris may also be thrown out as a result of the blast from a vapor cloud explosion.

The probability of occurrence of vapor cloud explosions appears to be rather low, based on analysis of the literature. EPA reviewed factors that may affect the probability of occurrence of a vapor cloud explosion, including the quantity of flammable vapor in a cloud, the presence of obstacles or partial confinement, and the type of ignition source. Analysis of accidents indicates that vapor cloud explosions are less likely when the quantity in the cloud is less than 10,000 pounds. It is generally thought that some type of obstruction or confinement enhances the probability that a vapor cloud explosion, rather than a vapor cloud fire, will occur. A high energy ignition source also contributes to the probability of occurrence of a vapor cloud explosion.

EPA carried out consequence modeling for fires and explosions of a number of flammable substances, using several PC-based modeling systems and hand calculation methods. Modeling results were used to estimate the greatest distance at which people potentially could be killed or injured by explosions or fires of flammable gases or liquids. The modeling indicated that, for a given quantity of a flammable chemical, vapor cloud explosions may have the greatest potential for offsite consequences. This result is consistent with information presented in the literature. Modeling indicated that BLEVEs may also, in some cases, have the potential for offsite consequences. Modeling results for pool fires and jet fires

indicated that thermal radiation effects extend for much shorter distances than for BLEVEs, for a given quantity of chemical.

Additional modeling was carried out based on actual vapor cloud explosions, and the results were compared with the results of the actual incidents. In general, it was found that the modeling results were in reasonable agreement with the results of the incidents. It was noted, however, that the specific circumstances surrounding an accident may have a significant effects on the severity and range of consequences of the accident. Modeling cannot take all circumstances and conditions into account.

Based on modeling and analysis of the literature, flammable gases and volatile flammable liquids appear to be the flammable substances of most concern, because they may readily form vapor clouds, with the potential for damaging vapor cloud explosions. EPA identified a number of such substances of concern. The analysis carried out by EPA for this report was intended to provide general background on the hazards of flammable gases and liquids. The modeling results and accident data illustrate and compare the consequences of vapor cloud explosions, vapor cloud fires, BLEVEs, and pool fires. This analysis does not provide a basis for determining the hazard posed by any flammable chemical in a specific situation.

## FLAMMABLE GASES AND LIQUIDS AND THEIR HAZARDS

### 1.0 Introduction

When the Emergency Planning and Community Right to Know Act (EPCRA), also known as Title III of the Superfund Amendments and Reauthorization Act (SARA), was enacted in 1986, a list of extremely hazardous substances (EHSs) (formerly the list of Acutely Toxic Chemicals published in November of 1985) was published under Section 302 of Title III. Section 302 requires a facility that has an EHS above its threshold planning quantity (TPQ) to notify the State Emergency Response Commission (SERC) that it is subject to the requirements for emergency planning.

The original list of EHSs was created using only acute toxicity criteria. The purpose of the list was to identify those substances that, if accidentally released, could cause death or serious irreversible health effects from toxicity off-site after a short exposure. However, toxicity is not the only hazard posed by chemicals. SARA states that the Administrator may revise the list, but such revisions "shall take into account the toxicity, reactivity, volatility, dispersibility, combustibility, or flammability of a substance."

The purpose of this report is to assess the potential consequences of accidents involving flammable chemicals. A particular emphasis is placed on assessing the impacts of accidents on communities neighboring industrial facilities.

The general approach taken in assessing the consequences of potential accidents involving flammable chemicals was to identify and evaluate: 1) existing listing and classification systems, along with any applicable criteria; 2) existing regulations and codes dealing with flammable materials; and 3) histories of accidents involving flammable materials. EPA's evaluation is discussed in Sections 3 and 4.

None of the above supplied sufficient information to serve EPA's specific needs. It was, therefore, decided to model the potential consequences from accident scenarios involving flammable chemicals to establish physical and chemical properties that may be indicative of the hazards associated with these chemicals. The results of the consequence modeling were then analyzed. The modeling is discussed in Sections 5 through 9. EPA's analysis of the modeling results is discussed in Section 10.

### 2.0 Background

EPA originally developed the list of EHSs as part of the voluntary Chemical Emergency Preparedness Program (CEPP) which was designed to increase public awareness of chemical hazards in communities and to focus effort on emergency planning. EPA believed that communities needed a starting point and intended that the list draw attention to the substances and facilities that pose the most immediate concern based on toxicity from an emergency planning and response perspective. EPA recognized and emphasized that there are tens of thousands of compounds and mixtures in commerce that may pose a hazard under specific circumstances and that this list addressed lethality and serious irreversible health effects associated with acute toxicity. The Agency chose lethality because it represents the most immediate concern in an emergency situation.

Several commenters on the rulemaking for the EHS list noted that physical/chemical hazards such as flammability or explosivity may lead to lethal consequences. In an official inquiry to the Agency in 1987, Senator Frank Lautenberg also noted concern for hazards other than toxicity and asked that EPA focus on other hazards. The Agency agreed and noted its intent to evaluate hazards other than toxicity in the future.

A Physical/Chemical Criteria Workgroup (P/C Workgroup) was formed at EPA to address the concerns raised by Senator Lautenberg and others and to focus on the problem of identifying materials which are hazardous based upon their physical/chemical properties and could thereby be candidate EHSs. The Workgroup initially considered the hazards referred to in the Act and determined that they fell into two general categories: hazards related to toxic properties and hazards related to physical/chemical properties. The characteristics of reactivity, volatility, dispersibility, combustibility, and flammability, mentioned in the Act, are related to a variety of physical/chemical properties; the Workgroup chose to focus on the physical/chemical properties that lead to the greatest potential hazards to people. Hazards associated with physical/chemical properties are primarily based on two phenomena that can cause serious personal injury or death. These phenomena are the result of the release of energy from highly reactive or flammable chemicals and are identified as overpressures from blast waves and thermal radiation from fires. Overpressures result from nearly instantaneous energy release, or detonation, while thermal energy is released during combustion, which occurs more slowly. Since explosive chemicals are highly reactive substances that can detonate and create overpressures, and flammable chemicals can burn and produce thermal radiation, the Workgroup focused on explosives and flammable chemicals as chemicals of concern.

The P/C Workgroup elected first to investigate what substances might have been identified and what criteria might already be in use by other organizations to characterize hazardous chemicals and to determine whether these criteria might meet EPA's needs. Criteria were investigated from many organizations including the National Fire Protection Association (NFPA), the United States Department of Transportation (DOT), the Occupational Safety and Health Administration (OSHA), and the European Economic Community (EEC).

The workgroup initially sought to evaluate and possibly use the criteria from these other organizations to develop options for adding to the list of EHSs chemicals that are flammable or explosive. The criteria from other organizations did not appear to be based on the consequences of an accident in terms of exposure to the community but rather on the consequences that could occur within the facility or during shipment of bulk materials or during fire-fighting. For example, an NFPA flammability rating of 4 is assigned to materials that will burn readily and that disperse readily or vaporize rapidly or completely at ambient conditions. This is important to fire-fighters approaching a fire involving a flammable material but gives little indication of the impact on a community from an accident that takes place inside an industrial facility.

The P/C Workgroup determined that an evaluation of the impacts of accidents involving substances that may be hazardous to the community because of certain physical/chemical properties was necessary. Such an evaluation would help to develop the criteria that would identify chemicals that should be considered extremely hazardous and therefore of concern for community emergency response planning efforts. One approach was to model accidents involving flammable chemicals and to analyze the resulting data in order to establish a correlation between the severity of accident consequences to the community and physical/chemical properties related to the consequences.

This approach is similar to the approach taken to establish the TPQs for the Section 302 EHSs listed based on toxicity criteria. These TPQs were established by assuming an accident scenario, a loss of containment of a specific toxic chemical, and then estimating the dispersion potential of each chemical. An index value based on the dispersion potential and toxicity was used to rank the chemicals, and chemicals were assigned to TPQ categories according to their ranking.

In its analysis of toxic substances under SARA section 302, EPA used a 100-meter fenceline distance to provide a guideline for community emergency planners to use in setting priorities for planning for hazards in the community. The 100-meter fenceline distance has also been used by the Occupational Safety and Health Administration (OSHA) in its analysis for thresholds for chemicals listed in its Process Safety Management Standard and by the state of Delaware for thresholds under its prevention regulations.

EPA recognizes that this distance may not be appropriate for protection of emergency responders. There is no absolute distance that would guarantee the safety of first responders in every situation.

The workgroup elected to segregate the chemicals into separate categories for flammables, explosives, and reactives for purposes of analysis and possible regulation even though it was recognized that there may be overlap of the consequences; e.g., a detonation of a flammable material may yield the same results as an explosion of a commercial explosive. However, the workgroup wanted to determine what parameters distinguish an extremely hazardous flammable substance from all other flammables, extremely hazardous explosives from all other explosives, and so on. This report focuses on flammable gases and liquids. A separate document has been developed to address commercial explosives and their hazards.

### **3.0 Existing Classification Systems, Regulations, and Codes**

There are many organizations that have developed lists, definitions, and classifications related to flammable chemicals, including DOT, NFPA, EEC, OSHA, and EPA. Some organizations establish their classifications with qualitative descriptions, but most classifications are based on physical/chemical properties, usually flash point and boiling point. None of these classification systems appeared to be primarily based on potential hazards to the community from incidents involving releases of flammable chemicals from fixed facilities; therefore EPA decided that none of these systems was appropriate or specifically applicable to EPA's regulatory needs. The systems examined are described briefly in the following sections; more detail is presented in Appendix A.

EPA intends to pursue harmonization of regulatory activity among various agencies to the extent possible, recognizing the different purposes of the regulations under different agencies. Regulation under section 302 of SARA Title III is intended to provide information to community planners on substances at fixed sites that may be hazardous to the community. As noted below, the regulations and classification systems used by other agencies and organizations have other purposes.

#### **3.1 DOT Classifications**

DOT classifies flammable materials for shipping purposes under 49 CFR 172. This regulation lists materials DOT regards as hazardous for purposes of transportation and prescribes requirements for shipping papers, package marking, labeling, vehicle placarding, and types of containers and safety devices that must be used to transport a flammable material. Details of the DOT classifications for flammable materials are found in Appendix A.

The DOT hazard classifications are based on maintaining safety during transport, given the range of ambient conditions possible. The consequences in terms of "first response" to accidents involving these materials are addressed in DOT's Emergency Response Guidebook. This guide details generic isolation distances, recommended fire-fighting techniques, and other initial emergency actions for incidents involving these substances. However, DOT focuses on transportation safety rather than hazards from fixed sites.

DOT hazard classes and packing groups for flammable substances are generally based on flash point and boiling point ranges, as described in Appendix A. However, for substances that are flammable and toxic, the packing group may be modified to reflect the additional hazard of toxicity; therefore, the DOT classifications of such substances may not provide a measure of their flammability.

#### **3.2 NFPA Classification Systems**

The NFPA has a flammability rating scale of 0 to 4, where 0 represents the lowest degree of flammability, for purposes of fire-fighting and fire prevention. The ratings are usually noted on Material

Safety Data Sheets (MSDSs) and are included in a standard that applies to facilities for manufacturing, storage, or use of hazardous materials. Approximately 1,500 chemicals have been assigned NFPA ratings. The classifications are designed to give "a general idea of the inherent hazards of any material and the order of severity of these hazards as they relate to fire prevention, exposure and control" (NFPA 1984).

NFPA has also developed a code (NFPA 30, Flammable and Combustible Liquids Code) concerning flammable and combustible liquids which is part of the National Fire Code and is specifically intended to be referenced by public authorities in laws, ordinances, regulations, and administrative orders. It was originally written as a model municipal ordinance for storing, handling, and using flammable liquids at fixed facilities. This code includes classifications based on flash point and boiling point. The NFPA flammability ratings and classifications from the NFPA code are discussed further in Appendix A.

### 3.3 EEC Classification Scheme

The EEC published a Council Directive on June 24, 1982, "concerned with the prevention of major accidents which might result from certain industrial activities and with the limitation of their consequences for man and the environment" (EEC 1982). The directive includes a list of toxic and explosive chemicals and several categories of flammable chemicals; the flammable categories are defined by "Indicative Criteria." Facilities that have listed chemicals in quantities greater than a specified threshold amount are required to report and meet a variety of conditions including performing hazards analyses and preparing emergency plans. The thresholds for the flammable categories are 200 metric tons (440,000 pounds) for flammable gases and flammable liquids under hazardous processing conditions, and 50,000 metric tons (1.1 million pounds) for other highly flammable liquids. The EEC Directive does not include a list of chemicals that fall into the various flammable categories. The indicative criteria related to flammability are discussed in Appendix A.

### 3.4 Regulations and Codes Applicable to Flammable Chemicals

Several agencies regulate flammable chemicals. OSHA regulates flammable and combustible liquids (29 CFR 1910.106), with handling and storage requirements and specifications for storage tanks. Specific requirements are included for bulk plants, service stations, processing plants, refineries, chemical plants, and distilleries. In addition, there are specific regulations dealing with acetylene (29 CFR 1910.101), hydrogen (29 CFR 1910.102), and liquefied petroleum gases (29 CFR 1910.110).

Under the Clean Air Act Amendments of 1990, OSHA was required to promulgate regulations intended to prevent accidental releases of chemicals which could pose a threat to employees. OSHA has published a standard, as described below. EPA is required to develop regulations for protection of the public, as discussed below.

OSHA has developed a chemical process safety management standard (57 FR 6356, February 24, 1992) that applies to any process involving a highly hazardous chemical at or above a specified threshold quantity. The requirements of this standard also apply to processes that involve flammable gases and flammable liquids in quantities of 10,000 pounds or more. Liquids stored below their boiling points under ambient pressure, without refrigeration, are exempt from the requirements. The OSHA Process Safety Management Standard is intended to protect employees by preventing or minimizing the consequences of catastrophic releases of toxic, reactive, flammable, or explosive chemicals. The requirements include development of a compilation of written process safety information; process hazards analysis, carried out by a team with expertise in engineering and process operations; development of written operating procedures for processes involving highly hazardous chemicals; employee training; pre-startup safety reviews for new and significantly-modified facilities; maintenance of mechanical integrity of critical equipment; and establishment of procedures for management of changes to process chemicals, technology,



equipment, and procedures; investigation of incidents; emergency action plans; and compliance and safety audits to ensure programs are in-place and operating properly.

Section 112(r) of the Clean Air Act (CAA) requires EPA to develop a list of at least 100 regulated substances that, when released, can cause death, injury, or serious adverse effects to human health or the environment. EPA proposed a rule listing regulated substances and associated thresholds on January 19, 1993 (85 FR 5102). The proposed rule includes a list of 68 flammable gases and volatile flammable liquids at a threshold of 10,000 pounds. The listed flammable chemicals meet the flash point and boiling point criteria for NFPA 4 (see above) and are considered the substances with the highest potential for involvement in vapor cloud explosions (see Section 6.1). In addition, substances proposed for regulation include 100 toxic chemicals, as well as commercial explosives as defined by DOT in Division 1.1. Facilities that use these chemicals above threshold quantities developed by EPA need to comply with new CAA regulations on release prevention, detection, and emergency response. One accident prevention provision of the CAA mandates the development of regulations requiring facilities to prepare and implement risk management plans. EPA is currently developing risk management plan regulations.

Flammable and combustible liquids may also be regulated by state or local governments; e.g., NFPA 30, Flammable and Combustible Liquids Code (see section 3.2), may be adopted or incorporated into law. DOT regulations include shipping requirements for flammable materials (49 CFR 172 and 173). All of these regulations are highly specific and deal with containers, pipes, and storage, handling, or transfer conditions in specified circumstances; however, none is directly applicable for EPA's purposes.

Gasoline is a flammable chemical of particular interest because of the high volumes in commerce and the many locations where it may be found. Therefore, EPA investigated the regulations for flammable chemicals with additional focus on gasoline. Gasoline is not regulated as a special case under any of the regulations or codes mentioned above. DOT's requirements for gasoline are similar to those for other liquids with similar properties, as are NFPA's recommendations for gasoline. OSHA's regulations for service stations do not mention gasoline specifically, but refer only to flammable liquids. These regulations cover the storage and dispensing of flammable liquids, electrical and heating equipment in areas with flammable liquids, waste handling, and fire extinguishers at service stations. Further information on the OSHA regulations for flammable liquids may be found in Appendix A. EPA's review of current regulations indicates gasoline is not considered a special case.

Fuels are not included as hazardous substances under CERCLA; "petroleum, including crude oil or any fraction thereof, ...natural gas, natural gas liquids, liquefied natural gas or synthetic gas usable for fuel (or mixtures of natural gas and such synthetic gas)" are not included in the definition of hazardous substances (40 CFR 300.6).

#### **4.0 Past Fire and Explosion Incidents Involving Flammable Chemicals**

EPA decided to review accidents involving flammable chemicals that have occurred in the past and their impact on the community to determine whether trends could be identified that would aid in identifying flammable chemicals that may be particularly hazardous to the community. The results of EPA's review are presented in this section.

##### **4.1 Acute Hazardous Events Data Base**

The Acute Hazardous Events Data Base (AHE/DB) was developed by EPA to provide a historical perspective on accidents that involve releases of hazardous substances in the United States (U.S. EPA 1988). The 1988 version of the data base includes data on 5,827 incidents that occurred between the 1960s and 1987 (the majority of the incidents appear to have occurred in the 1980s). Information in the data base is from the National Response Center, press reports, and several state offices. This data base was

reviewed to identify accidents specifically involving flammable chemicals and evaluate the consequences of these accidents, if possible, in terms of physical/chemical characteristics and the specific hazards posed to the surrounding community.

The AHE/DB indicates that flammable chemicals have been involved in numerous accidents that resulted in fires and explosions, and these accidents led to many deaths and injuries. However, the data are not sufficiently specific to serve as a basis for identifying chemicals that may be extremely hazardous based on their physical/chemical properties.

Fire and explosion incidents account for about 13 percent of the total incidents in the AHE/DB, but they account for nearly 92 percent of the deaths and about 36 percent of the injuries reported. However, the number of these deaths and injuries that occurred on-site and the number that occurred off-site cannot be differentiated in the data base; therefore, the degree of impact these incidents had on the surrounding community cannot be accurately determined. Additional details and analyses using the data from the AHE/DB may be found in Appendix F.

#### **4.2 Accidental Release Information Program**

EPA's Accidental Release Information Program (ARIP) data base contains 2,200 records (as of June, 1992) with questionnaire information from facilities on the causes and consequences of accidental releases and on release prevention procedures and equipment. Flammable chemicals included in the ARIP data base are either CERCLA hazardous substances or EHSs. Facilities must complete the ARIP questionnaire if the release meets at least one of the following criteria:

- 1) The quantity released was above a certain multiple of the CERCLA Reportable Quantity (RQ);
- 2) The release resulted in a death or injury;
- 3) The release was one in a trend of frequent releases from the same facility; or
- 4) The release involved a chemical listed by EPA as an EHS.

Of the data bases reviewed, only the ARIP data base maintains information on off-site deaths, injuries, or evacuations. Based on analysis performed on 2,200 ARIP records, six events have been listed as explosive incidents involving flammable chemicals. None of the six caused a public death or injury. One ARIP release and explosion of propylene caused two worker injuries and evacuation of 150 members of the public. In one incident, explosion of silane gas resulted in the deaths of two facility workers. Appendix F provides additional information on these six releases.

#### **4.3 OSHA Data Base**

The OSHA data base contains records of OSHA accident inspections. These inspections were conducted in response to a worker death, at least three worker injuries, or reporting of workplace hazards. The most recent and complete data base records for OSHA inspections (fiscal year 1990) were examined for this analysis. Analysis of the data indicate that 32 incidents involving flammable chemicals resulted in 25 deaths of workers and 43 injuries to workers (OSHA 1990). See Appendix F for more information on these releases.

#### **4.4 Fatal Hazardous Materials Accidents Database**

The Fatal Hazardous Materials Accidents Database, developed by Resources for the Future, contains information on fatal accidents which involved the release of hazardous materials. Data were obtained from encyclopedias, almanacs, books, reports, articles, newspapers and computer files (including AHE/DB). The database contains reported accidents which occurred during industrial production, storage, handling and transportation of hazardous materials. Only those accidents involving at least one reported death for U.S. accidents and five reported deaths for accidents outside the U.S. are included. Every such event between 1945 and 1991 is in the database, with the following exceptions: mining or mineral extraction accidents; handling, transportation, and storage of munitions, fireworks, and manufactured explosives (manufacture of such products was counted); and transmission and distribution of natural gas (i.e., pipelines).

There are 1,068 accidents reported in the database, of which 758 occurred in the U.S. Fifty-six percent of these fatal accidents involved a fire or explosion of a flammable material. Explosions of flammable substances accounted for 412 accidents, and fires (excluding fires involving explosives) accounted for 188 accidents in the database. Approximately 14 to 25 thousand injuries, and eight to 12 thousand deaths were associated with these accidents. The database does not distinguish between on-site and off-site injuries and fatalities. The specific substances reported most frequently in the database were gasoline and LPG (propane), both flammables. The types of reported fires and explosions of flammable substances in the database included 55 unconfined vapor cloud explosions, 43 confined vapor explosions, 48 fireballs, 22 BLEVEs, and 11 detonations of flammable substances. In a number of cases, two of these types of events were reported for the same incident (e.g., unconfined vapor cloud explosions and BLEVEs were reported in three incidents, unconfined vapor cloud explosions and fireballs were reported in seven incidents).

#### **4.5 Major Hazard Incident Data Service (MHIDAS)**

The Major Hazard Incident Data Service (MHIDAS) is a world-wide databank maintained by the Safety and Reliability Business (SRD) of AEA Technology and the UK Health and Safety Executive. It is continually updated, and records and analyzes incidents involving hazardous materials that resulted in or had the potential to produce an off-site impact. Off-site impact includes incidents which involved evacuation and those which could, but for mitigating circumstances, have led to evacuation, casualties, or damage to property or the environment.

MHIDAS currently contains over 6,500 records with information on incidents involving hazardous substances. Nearly 5,000 of these records involve fires or explosions or the threat of fire (e.g., a flammable material was involved in the incident. Types of fire or explosion incidents, their frequency in the database, and the number of records in which deaths, injuries, or evacuations were reported for flammable substances shown in the table on the next page.

As the table shows, it appears that a somewhat higher percentage of unconfined vapor cloud explosion records in the database include reports of deaths, injuries, or evacuations, with an even higher percentage for deaths, than the other types of fires and explosions. However, it should be noted that the numbers reported above do not precisely reflect the number of incidents reported. Because reported incidents may have involved multiple fires or explosions, the numbers presented reflect some overlap. In addition, if several substances were involved in an incident, there may be multiple records for that incident in the database.

Type of Incident	Number of Records	Number with Deaths, Injuries, or Evacuations	Number with Deaths
Confined explosions involving flammable substances	197	136 (69 percent)	72 (37 percent)
Unconfined vapor cloud explosions	110	89 (81 percent)	63 (57 percent)
BLEVEs involving flammable substances	111	84 (76 percent)	41 (37 percent)
Fireballs	98	72 (73 percent)	34 (35 percent)
Vapor or flash fires	96	72 (75 percent)	51 (53 percent)
Pool fires	113	73 (65 percent)	39 (35 percent)
Jet fires	15	8 (53 percent)	5 (33 percent)

#### 4.6 M & M Protection Consultants Data Base

The M & M Protection Consultants document entitled Large Property Damage Losses in the Hydrocarbon-Chemical Industries - A Thirty-Year Review describes 100 incidents involving large property damage losses. Offshore and marine transportation incidents are excluded. Because the data base focuses on hydrocarbon-chemical incidents, it covers many accidents involving flammable chemicals. Most of the incidents involve fires or explosions. Vapor cloud explosions account for 44 of the 100 incidents in the M & M data base. The document notes, "The vapor cloud explosion ... has become established as the mechanism most frequently leading to catastrophic losses in the hydrocarbon processing and chemical industries" (M & M 1990). Vapor cloud explosions are discussed more fully in Section 6.1.

The M & M data base is particularly valuable in providing information on the consequences of vapor cloud explosions on the community nearby a facility. Spanning thirty years, the data include descriptions of explosion and fire events, the causes of the property loss, and the estimated costs of property damages. Information specifically related to consequence analysis includes quantity released, temperature and pressure of chemical released, overpressures created by an explosion, projectile distances, vapor cloud size, flashback distances, and property damage. Unfortunately, data on death and injury are not available in the data base as provided. Appendix F provides additional information on incidents in the M & M data base.

Of the data bases consulted, the M & M data base provides the most complete information on the circumstances and the off-site consequences of flammable chemical incidents, particularly on vapor cloud explosions. However, the small number of incidents over a thirty year period is not sufficient for EPA to identify or classify flammable chemicals that pose hazards to the community.

#### 5.0 Accident Consequence Modeling

Because current classification methods and regulatory approaches used by various organizations (e.g., DOT, NFPA, EEC, OSHA, etc.) are not oriented to addressing the hazards posed to the community from flammable chemicals and because accident data also are not sufficient for identifying or classifying the hazards of flammable chemicals, EPA decided to use modeling techniques to evaluate potential hazards

to the community from incidents involving release of flammable liquids and gases from fixed sites. No single hazards analysis model has been universally accepted; therefore, three PC-based models and several methods involving manual calculations were used for a single release quantity to estimate consequences of accidents involving flammable liquids and gases for comparison purposes. As will be discussed in the following section, the WHAZAN model was selected for use in the accident consequence analysis for a range of quantities and chemicals.

The remainder of this section provides an overview of various models available. Section 6 discusses the different types of flammable chemical fires and explosions. Section 7 examines how certain characteristics of flammable chemical accidents (e.g., confinement, delayed ignition) will qualitatively affect the modeling results. Additionally, inputs for consequence models are discussed. Section 8 examines the hazards criteria used for evaluating the consequences of different types of flammable chemical incidents. Section 9 provides the results of the modeling runs, including WHAZAN results using data from actual vapor cloud explosions and a comparison of the WHAZAN results with the actual results of the incidents. Section 10 details EPA's findings.

EPA did not attempt to evaluate the models used or to estimate uncertainties in modeling results. The results obtained using the various methods are presented for comparison purposes in Appendix D. In general, the various methods show reasonable agreement in predicting consequences for various accident scenarios and hazard criteria levels. Additional information on each of the models is presented in Appendix B. Assumptions used in the modeling and the physical/chemical data required as input are summarized in Appendix E.

### 5.1 WHAZAN Methodology

The commercially available World Bank Hazard Analysis (WHAZAN) computer system is a group of computer programs capable of performing quick estimates of the possible hazardous consequences of accidental releases of toxic and/or flammable gases or liquids. It was developed by Technica International Ltd. in collaboration with the World Bank. These programs comprise several models which can calculate the consequences of different types of chemical accidents. The models derive their inputs from a data base which contains relevant properties of some hazardous chemicals. The user can add chemicals and properties to the data base. A user of WHAZAN can either run one of the models individually (stand-alone models) for calculating the hazardous consequences from a specific type of event (e.g., vapor cloud explosion), or can link two or more models in a way such that outputs from one model can be used automatically as inputs for another model (linked models). The models provide information about four key areas: outflow of the chemical from its container, behavior immediately after release, dispersion after release, and fires and explosions. The WHAZAN system is extensively used by large international chemical companies and government agencies.

WHAZAN makes certain assumptions regarding atmospheric behavior and accidental release rates of various gases and liquids. Comparison of WHAZAN results with the results using other methods showed reasonable agreement. Also, WHAZAN results presented in section 9.1 largely agree with consequence data from actual vapor cloud explosions. Therefore, WHAZAN was used as the primary method of consequence analysis for flammable chemicals. More details on the WHAZAN model and its theoretical basis are found in Appendix B.

### 5.2 ARCHIE Methodology

Accident hazard assessment and consequence analysis procedures have been incorporated into a system developed for the Federal Emergency Management Agency (FEMA), DOT, and EPA, entitled Automated Resource for Chemical Hazard Incident Evaluation (ARCHIE). The primary purpose of ARCHIE is to provide emergency personnel with several integrated estimation methods that may be used

to assess the vapor dispersion, fire, and explosion impacts associated with episodic discharges of hazardous materials into the environment. The program also is intended to facilitate a better understanding of the nature and sequence of events that may follow an accident and the resulting consequences.

The core of the ARCHIE computer program is a set of hazard assessment models that can be sequentially utilized to evaluate consequences of potential discharges of hazardous material and thereby assist in the development of emergency plans. ARCHIE can help emergency planning personnel understand: 1) the nature and magnitude of hazards posing a threat to their jurisdiction; 2) the sequence of events that must take place for these threats to be realized; and ultimately 3) the nature of response actions that may be necessary to mitigate adverse impacts upon the public and its property in the event of an emergency.

The system contains numerous models for evaluating different types of incidents and their consequences, e.g., pool fires, unconfined vapor cloud explosions, and fireballs. More details about the system and its theoretical basis are presented in Appendix B.

### 5.3 The "Yellow Book" Methodology

The Bureau of Industrial Safety (TNO) of the Netherlands has issued a report, commissioned by the Directorate-General of Labour, entitled "Methods for the Calculation of the Effects of the Escape of Dangerous Material" (March 9, 1980), also known as the "Yellow Book." Equations and calculation methods for estimating the effects of several types of accidents involving flammable liquids and gases are presented. Some of these methods were used as the basis for models in WHAZAN. The Yellow Book includes calculations for pool fires, vapor cloud fires, and vapor cloud explosions for gases, and pool fires and vapor cloud fires for liquids. For gases, two different methodologies are used for vapor cloud fires: the flashed fraction of each gas is modeled as an instantaneous release; the non-flashed fraction is modeled as a continuous release from an evaporating pool. In both cases, dispersion as a neutrally buoyant cloud is assumed. The flashed fraction of each gas is used to calculate the vapor cloud explosion results. Since there is no calculated flashed fraction for liquids, no vapor cloud explosion results appear for liquids. Appendix B presents details of the calculations that were used in this analysis.

### 5.4 AIChE-Sponsored Course Materials

The American Institute of Chemical Engineers (AIChE) sponsored course material titled, "Methods for Calculation of Fire and Explosions Hazards" (1987), presents equations for calculating the effects of several types of accidents involving flammable liquids and gases. This material is a compendium of methods and algorithms dealing with fires and explosions, not a straightforward approach to determining consequences of various accident scenarios. The equations used in this analysis and details of the methodology are presented in Appendix B.

### 5.5 The "Green Book" Methodology

EPA, in conjunction with FEMA and DOT, developed the "Technical Guidance for Hazards Analysis" (1987) to provide guidance to local emergency planning committees (LEPCs), local emergency agencies, and community groups in assessing hazards related to potential airborne releases of extremely hazardous substances listed because of their toxicity under section 302 of SARA Title III. This guidance, known as the "Green Book," provides methods for estimating chemical releases and dispersion distances. These methods were applied to the airborne dispersion of vapor clouds of flammable liquids and gases to estimate distances for vapor cloud fires. Appendix B contains details of these calculations.

## 5.6 PHAST Methodology

PHAST (Process Hazard Analysis Software Tool) is a software package developed by Technica International Ltd. and Rohm & Haas. Technica also developed WHAZAN for the World Bank. In fact, PHAST uses the same algorithms as WHAZAN for predicting consequences. PHAST, like WHAZAN, is designed to estimate the consequences of accidental releases of toxic or flammable liquids and gases. Unlike WHAZAN, PHAST is a PC-based version of SAFETI (Software for Assessing Flammable, Explosive, and Toxic Impact) a mainframe-based hazard analysis system owned by Technica. PHAST is used by Technica to evaluate potential changes to SAFETI, and therefore represents one of the most current hazard modeling packages. The PHAST package includes a data base of 56 commonly used chemicals; additional chemicals may be entered. The PHAST system can be used for estimation of the effects of BLEVEs, pool fires, jet flames, flash fires, and vapor cloud explosions.

There are some important differences between PHAST and WHAZAN. PHAST incorporates the TECJET model, a proprietary dispersion model developed by Technica. TECJET provides algorithms which simulate aerosols, overflows, and gas dispersion in PHAST. TECJET is a three dimensional dispersion model which accounts for perturbation around the center line axis of a release caused by a crosswind. WHAZAN does not have this capability. Unlike WHAZAN, the models in PHAST cannot be run independently as stand-alone models, but are completely integrated to run in sequence. PHAST includes algorithms which maintain strict thermodynamic control during the modeling. This prevents unrealistic modeling runs such as calculating a vapor cloud explosion when thermodynamic conditions dictate that the release will not form a vapor cloud.

## 5.7 Multi-Energy Model

A.C. van den Berg and others from TNO introduced the multi-energy concept for vapor cloud explosions (van den Berg 1985; van den Berg et al. 1991). In contrast to the TNT equivalence concept where the entire vapor cloud is treated as a potential source of a vapor cloud explosion, the multi-energy method is based on the principle that only partially confined areas in the cloud are likely to contribute to blast generation. Each such area is treated separately. The initial blast strength for each area is expressed as a number ranging from one to ten, depending on degree of confinement and obstruction; a factor of ten applies to a detonation. The total combustion energy involved and the initial blast strength are used to derive a distribution of blast parameters in the vicinity of the gas explosion. A mathematical model has been developed to solve equations describing convective and diffusive transport of flow. Small scale experiments were carried out, and the results were compared with results from the model. A research program on this method is still being carried out (van den Berg et al. 1991).

Some drawbacks of the multi-energy method have been noted. Lenoir and Davenport (1993) suggest that many variables need further evaluation, including degree of confinement, initial blast strength, and strength of ignition sources. In addition, the multi-energy method only applies to quiescent vapor clouds, not to explosively dispersed clouds (Lenoir and Davenport 1993).

The multi-energy model appears to be more complex than the PC-based models and calculations discussed in the previous sections. Results depend on site-specific factors such as obstructions present, which are not considered in the other models; therefore, it would be difficult to compare results from this model to results from the other models. Calculations based on this method cannot be carried out without a computer program; EPA has not attempted to obtain such a program and has not included the multi-energy method in this analysis.

### **5.8 New Jersey Method for Fireballs**

The New Jersey Department of Environmental Protection and Energy has developed a computation method for calculating quantity-distance relationships for the thermal effects of fireballs from Boiling Liquid Expanding Vapor Explosions (BLEVEs). New Jersey has developed a computer program, "ACTOR Model Thermal Energy Analysis Subroutine," to carry out the calculations (NJDEPE 1991). A review of this method indicated that it is similar to the WHAZAN and ARCHIE methods for estimating effects of BLEVEs.

## **6.0 Types of Flammable Chemical Fires and Explosions**

There are several types of flammable chemical incidents that may have consequences for the community. Among the literature sources examined, there appears to be a general consensus regarding the types of events resulting from releases of flammable substances. These include vapor cloud explosions, vapor cloud fires, BLEVEs, pool fires, and jet fires, as discussed in the following sections. The hazards posed to the public from these events are also described below, as well as factors (e.g., quantity released, degree of confinement) that influence the probability of occurrence and the severity of the consequences of the explosion or fire. The hazards of projectiles resulting from explosions are also discussed.

### **6.1 Vapor Cloud Explosions**

Volatile materials can form vapor clouds when they are released in an uncontrolled manner from containment vessels. Materials that are at elevated temperatures and/or pressures are particularly of concern. Released volatile, flammable materials can flash directly into the vapor state and/or flow to the ground and form a pool of liquid which subsequently evaporates to form a vapor cloud. After a vapor cloud is formed, three things can happen: it can disperse and have no fire or explosion impact on neighboring communities; it can ignite and burn (vapor cloud fire); or it can detonate or explode and cause high pressure shock waves. According to Kletz (1977), unconfined vapor cloud explosions almost always result from the release of flashing liquids (i.e., liquids under pressure at temperatures above their boiling points). For a vapor cloud to ignite and burn or explode, its concentration in air must be within its flammable limits.

Chemicals are vaporized much more rapidly by boiling than by evaporation; therefore, chemicals with boiling points below ambient temperatures volatilize very rapidly after being spilled and are more likely to generate high-mass clouds than chemicals that boil above ambient temperatures. Chemicals that are gases at ambient temperatures therefore represent a greater explosion hazard than less volatile chemicals with boiling points greater than ambient temperatures (liquids and solids). However, vapor clouds may also be formed by higher-boiling liquids (e.g., cyclohexane) released at temperatures above their boiling points.

An exemplary list of chemicals that are known to have been involved in vapor cloud explosions is shown in Exhibit 1. Note that 12 of the 15 chemicals listed are gases under ambient conditions.

Exhibit 2 summarizes information on a number of incidents that resulted in vapor cloud explosions. These incidents are cited in later sections to illustrate the effects of various factors that may influence the outcomes of incidents involving flammable chemicals. In cases where there were sufficient data, modeling was carried out using reported data from selected incidents as model input. The modeling effort and the results obtained are discussed in Section 9.2.



**Exhibit 1**  
**CHEMICALS KNOWN TO HAVE BEEN INVOLVED IN VAPOR CLOUD EXPLOSIONS**

<u>Chemical</u>	<u>Boiling Point (°C)</u>
Hydrogen	-253
Methane/LNG	-161
Ethylene	-102
Propylene	-46
Dimethyl Ether	-43
Propane	-42
Vinyl Chloride	-24
Isobutane	-14
Isobutylene	-12
Butadiene	-8
Ethylene Oxide	11
Ethyl Chloride	12
Gasoline	59
Hexane	72
Cyclohexane	81
References:	R.W. Prugh (1987) J. Skarka (1987)

**Exhibit 2**  
**SAMPLE QUANTITIES INVOLVED IN VAPOR CLOUD EXPLOSIONS**

<b>Facility</b>	<b>Chemical</b>	<b>Quantity in Cloud (pounds)</b>
Quebec, Canada	styrene	1,500
New Castle, DE	propylene	12,000 - 16,000
Texas City, TX	hydrocarbons	20,000
Norco, LA	hydrocarbons (propane)	20,000
Doe Run, KY	ethylene oxide	45,000
Flixborough, England	cyclohexane	60,000 (spilled)
Lake Charles, LA	isobutane	80,000 (spilled)

Source: M & M Data Base, 1990

Vapor cloud explosions can be extremely destructive incidents that can have both on- and off-site impacts. Usually, the high pressure or overpressure created by the explosion is responsible for the damage. In addition, projectiles (e.g., container fragments, debris from damaged buildings) can cause damage and injury (see Section 6.6 for a discussion of projectiles).

#### **6.1.1 Effect of Quantity on Probability of Vapor Cloud Explosions**

According to Prugh (1987), the probability of a vapor cloud exploding appears to depend on the weight of flammable vapor in the cloud (i.e., the quantity in the cloud above the lower flammability limit). Prugh's analysis (based on actual vapor cloud explosion events) indicates that the probability of explosion is 50 percent when the weight of flammable vapor is 90,000 kilograms (200,000 pounds); the probability decreases with decreasing weight. Based on an equation developed by Prugh, for vapor clouds containing less than 10,000 pounds of flammable vapor, the probability of explosion becomes relatively low (approximately 7 percent for 10,000 pounds and less than 1 percent for 1,000 pounds). Prugh's probability analysis considered only the likelihood of a vapor cloud exploding following a release, not the likelihood that a release might occur.

The American Petroleum Institute (API) has developed recommended process hazard management practices (including such topics as safety reviews, hazards analyses, training, safe practices, and incident investigation) for production and refining departments (API Recommended Practice 750). This document has an appendix detailing the application of the recommended practice to facilities that have the potential to release five tons (10,000 pounds) of gas or vapor in a period of a few minutes. The five-ton quantity was chosen by API as a reasonable threshold on the basis of catastrophic potential and probability of explosion. For a vapor cloud containing five tons of hydrocarbon, API considers the probability of explosion to be about 5 percent, compared to less than 1 percent for one ton or less (API 1990).

Data from the M & M data base generally seem to support the 10,000-pound threshold for vapor cloud explosions (see Exhibit 2). The explosion in Canada involving 1,500 pounds may be an anomaly since it was a partially confined vapor cloud explosion. Vapor cloud explosions have occurred at quantities as low as 20 kg, but the damage they have produced has been very localized and of little concern regarding injuries and losses (Lewis 1980). Releases as great as 1,000 metric tons have been identified, but they have usually produced fires or firestorms. The rate of discharge has a large influence on air mixing. Rates of discharge lower than about 0.25 metric tons of fuel per minute do not seem to be a severe aerial explosion risk (Lewis 1980), probably because the low rate of release is unlikely to lead to accumulation of a cloud of vapor within the explosive limits.

#### **6.1.2 Confinement and Mixing in Vapor Cloud Explosions**

Presence of obstacles may confine the vapor cloud and consequently increase the concentration of the flammable substance in the vapor cloud. Upon deflagration or detonation, this increased concentration ensures flame acceleration and/or maximum overpressure achievement. In addition, the presence of objects in the cloud's path appears to affect the likelihood of explosion. Wiekema (1984) concludes that, "...when no sizable objects were in the cloud no explosions have been recorded, and that, in fact, the presence of obstacles and confinement is a necessary condition for an explosion to occur." Also, confined vapor cloud explosions or fires require less cloud mass than unconfined vapor cloud explosions or fires. Lewis (1980) reports that "significant" blast effects have occurred under semi-confined conditions for quantities as low as 100 kg (220 pounds); Lewis does not further describe the blast effects. One case in the ARIP database involved confinement and subsequent explosion of 1,000 pounds of propylene and propane (ARIP 1991).

A study by Prugh (1987) concludes that the occurrence of a vapor cloud explosion rather than a vapor cloud fire (both of which occur under similar circumstances) depends upon the location of the

ignition source and the amount of turbulence or mixing in the cloud. Skarka (1987) concludes that only the central zone of the cloud of vapors mixed with air inside the explosion limits can cause and contribute to the explosion.

According to the TNO Yellow Book (1980), the composition of vapor clouds is not the same at every point; there are concentration gradients and inhomogeneities. The effect of these concentration gradients and inhomogeneities on the flame acceleration mechanism of a detonation is not fully known. According to van den Berg et al. (1991), the inhomogeneity of vapor clouds resulting from an accidental release prevents the propagation of a detonation through the cloud in most cases; therefore, most vapor cloud explosions may be assumed to be deflagrations (van den Berg et al. 1991).

### **6.1.3 Energy of Vapor Cloud Explosions**

Many flammable gases have relatively high theoretical TNT equivalents compared to commercial explosives, where the TNT equivalent is the relative weight of trinitrotoluene (TNT) that produces the same effect as is produced at a given distance by the material under consideration. Commercial explosives generally have TNT equivalents between roughly 0.3 and 2. The theoretical TNT equivalent for flammable gases indicates the explosive potential, assuming the material explodes completely; calculated values reported by Prugh (1987) range from 4.5 (for vinyl chloride) to 34 (for hydrogen). For most hydrocarbons, the theoretical TNT equivalent is about 12 (Prugh 1987). However, in vapor cloud explosions, it appears that only a fraction of the vapor in the cloud explodes. (In contrast, for commercial explosives, most of the explosive material present is expected to be involved in the explosion.) For example, Prugh (1987) reports that for vapor cloud explosions of hydrocarbons, the observed TNT equivalent was 1.0, compared to the theoretical TNT equivalent of 12 (i.e., the actual explosive yield is eight percent of the theoretical yield. Lees (1980) reports that the fraction of the heat of combustion used to produce the blast wave is usually between one and 10 percent but that much higher explosion efficiencies have been reported. For modeling the consequences of vapor cloud explosions, a "yield factor" is applied to account for the unexploded vapor in the cloud.

### **6.1.4 Type of Ignition**

The energy supplied to the gas/air mixture per unit time and per unit volume by an ignition source is extremely important in determining whether ignition immediately results in a detonation or in a deflagration. Much greater energy is required for the initiation of a detonation. According to the TNO Yellow Book, the minimum ignition energy required for detonation is unknown for most gases, but the first test results for some hydrocarbon gases indicate that this value can vary by orders of magnitude.

### **6.1.5 Delayed Ignition Effects**

Time between failure of chemical containment and ignition of a vapor cloud can vary by incident (Exhibit 3) depending on the concentration of released vapors and the proximity of those vapors to an ignition source. Wiekema (1984) noted that "...an ignition within about one minute after the beginning of the release will enhance the possibility of an explosion." According to the M & M data base, the longest reported time before ignition (35 minutes) occurred in a facility in Feyzin, France. Seven mile-per-hour winds are thought to have been instrumental in directing the butane vapors away from facility ignition sources. The cloud was eventually ignited by an automobile on a road nearby the plant boundary (M & M Data Base 1990).

**Exhibit 3**  
**TIME BEFORE IGNITION**

<b>Facility</b>	<b>Time Between Failure and Ignition</b>
Pampa, TX	10 seconds
Norco, LA	30 seconds
Pasadena, TX	1 minute
New Castle, DE	1.5-2 minutes
Texas City, TX	2 minutes
Baton Rouge, LA	2 minutes
Mount Belvieu, TX	4-5 minutes
Pernis, Netherlands	6-8 minutes
Abqaiq, Saudi Arabia	7 minutes
Mexico City, Mexico	10 minutes
Feyzin, France	35 minutes (windy)

Source: M & M Data Base, 1990

Wiekema (1984) reported that over 60 percent of vapor cloud explosions are reported to result from ignition within 100 meters of the release site. However, some vapor clouds may not explode until an ignition source is found in a nearby community, possibly increasing the chance of off-site damage. Exhibit 4 shows a number of incidents in which vapor clouds ignited at some distance from the point of release.

Delayed ignition might allow more flammable vapor be released, and the vapor cloud might travel further off-site, possibly increasing the potential for off-site damage. However, the vapor cloud will also disperse with time. According to Kletz (1977), if ignition is delayed, the quantity within the explosive range will first increase and then decrease as the vapor disperses:

**Exhibit 4  
DISTANCE TO IGNITION**

Facility	Chemical	Distance to Ignition
Billings, MT	butane	30 m
Goi, Japan	propylene/hexane	45 m
Denver, CO	propane	90 m
Feyzin, France	butane	90 m
Texas City, TX	hydrocarbons	195 m
Abqaiq, Saudi Arabia	gas	450 m
Rio De Janeiro, Brazil	LPG	beyond facility boundary

Source: M & M Data base, 1990

## 6.2 Vapor Cloud Fires

Vapor cloud fires, also referred to as flash fires, do not generate extreme overpressures similar to vapor cloud explosions. Instead, the associated hazard is a rapidly moving flame front. The size of the vapor cloud is determined by the extent to which the released material disperses in the atmosphere before ignition. If a vapor cloud or plume contacts an ignition source at a point at which its concentration is within the range of its upper and lower flammable limits, a wall of flame may flash back towards the source of the gas or vapor (FEMA, DOT, EPA 1989). Following ignition of an over-rich cloud of fuel, a diffusion-type flame rolls back across the cloud of fuel as air is mixed further with the over-rich cloud until the entire cloud is burned (Lewis 1980). Individuals engulfed in such a vapor cloud that then ignites have a high probability of being killed. However, there were no reported fatalities beyond the actual vapor cloud due to radiation effects in a sample of vapor cloud fires examined by Wiekema (1984). He concludes that since the area outside of the cloud exposed to intense thermal radiation is small, no fatalities due to thermal radiation can be expected outside the area engulfed in flame.

One incident of a vapor cloud fire occurred at an Austin, Texas, pump station on February 22, 1973. Failure of a ten-inch pipeline carrying natural gas liquids (NGL) at 525 psig pressure caused the release and vaporization of 278,880 gallons of NGL onto a road adjacent to the pump station and into ditches adjacent to the road. Shortly after the release, two cars entered the vapor zone and stalled; the occupants of these vehicles immediately fled safely out of the vapor zone. Soon after, a van carrying six adults and two children stalled. The passengers exited the vehicle and the driver tried to restart the van's engine. A spark ignited the fuel-air mixture, immediately killing four of the van's occupants; two occupants later died of injuries sustained, while the other two were severely burned. All three vehicles were destroyed. A 2,400 foot long section of pasture land along the road was charred black (Eisenberg, 1975).

## 6.3 BLEVEs and Resulting Fireballs

Boiling Liquid Expanding Vapor Explosions (BLEVEs) occur when sealed tanks of liquid or gaseous hazardous materials are exposed to fire, which may cause excessive pressures within the tank

combined with weakening of tank walls. The sudden failure of the vessel and rapid vaporization and expansion of its contents is termed a BLEVE. BLEVEs also generally result in ignition of the vapor cloud when the substance is flammable, and a large rising fireball may form, the size of which will vary with the accident conditions and the type and amount of hazardous material present. Although the fireball is generally of short duration, the intense thermal radiation generated can cause severe and possibly fatal burns to exposed people over relatively considerable distances in a matter of seconds (FEMA, DOT, EPA 1989). Overpressures and container fragment projectiles also may be generated by BLEVEs but are of less concern than the thermal radiation (Nazario 1988). See Section 6.6 for a discussion of projectile hazards. For all major fuel release incidents studied which led to BLEVEs, the incident was accompanied by a major fire incident (Lewis 1980).

Lewis (1980) describes BLEVEs for fuels as follows:

When a pressure vessel containing a liquefied flammable gas or a flammable liquid is heated by an external fire which heats the metal wall at the vapor space level, the vessel will rupture into a number of large pieces which will rocket considerable distances as fuel inside the pieces burns. This is accompanied by a large fireball and some explosive pressure effects produced from the liquid rapidly expanding during the propagation of fractures as the vessel ruptures. These pressure effects are usually minor compared with the fires started by heat radiation.

The Center for Chemical Process Safety Guidelines for Chemical Process Quantitative Risk Analysis (CCPS 1989) describe a fireball as follows:

Fireball: The atmospheric burning of a fuel-air cloud in which the energy is mostly emitted in the form of radiant heat. The inner core of the fuel release consists of almost pure fuel whereas the outer layer in which ignition first occurs is a flammable fuel-air mixture. As buoyancy forces of the hot gases begin to dominate, the burning cloud rises and becomes more spherical in shape.

Nazario (1988) suggests a guideline that if 10% of a chemical vaporizes when it is released to the atmosphere from a vessel, the chemical has a high potential to BLEVE. Pentane and lighter hydrocarbons generally satisfy this vaporization criterion when contained in vessels at their typical storage temperatures and pressures and released to the atmosphere. Results produced by the models for chemicals heavier than pentane have therefore not been considered further in this assessment; however, it should be noted that it is not impossible for less volatile chemicals, when subjected to elevated temperature and pressure conditions, to result in BLEVEs.

BLEVEs are not always the principal cause of disaster but can occur secondarily when, for example, flames from an ignited vapor cloud impinge upon containers with flammables/explosive contents. Exhibit 5 contains a sampling of chemical incidents involving BLEVEs that have occurred in the last thirty years. In all of these incidents, other types of fires and explosions were associated with the BLEVEs.

Several catastrophic accidents have been classified as BLEVEs. One of the most notable was at a Mexico City liquefied petroleum gas (LPG) site where BLEVEs occurred involving millions of pounds of flammable gas and numerous tanks. Hundreds of residents in homes adjacent to the plant were killed.

**Exhibit 5**  
**INCIDENTS INVOLVING BLEVEs IN THE M & M DATABASE**

Incident Location, Date	Type of Facility	Cause/Description	Damage
Pasadena, TX (10/23/89)	Petrochemical Plant	Vapor cloud of ethylene and isobutane formed and ignited approximately one minute after release. Heat from fireball thought to have caused BLEVEs of neighboring pressure tanks.	\$500 to \$750M
Romeoville, Illinois (07/23/84)	Refinery	Explosion of released propane resulted in fire engulfing the unsaturated gas plant, FCC, and alkylation units. Fire burned out of control for about 30 minutes before a BLEVE occurred in a process vessel in the alkylation unit. One piece of debris thrown 500 feet cut pipelines and finally struck a tank in the water treatment unit. Another piece of debris was thrown 600 feet where it caused another major fire.	\$143.5M
Mexico City, Mexico (11/19/84)	Terminal	Release of LPG during transfer caused formation of LPG vapor cloud. Structures at the facility included six spheres and 48 bullets for a total storage capacity of more than 4.2M gallons of LPG. Within five minutes of ignition of the LPG vapor cloud, the first of a series of BLEVEs produced a fireball approximately 1200 feet in diameter. Heat and projectiles from the BLEVE released fuel from other tanks. Four of the six spheres (each with 420,000 gallon capacity and about half-full at time of transfer line rupture) and 44 of the bullets BLEVE'd or were ruptured by missiles. The two largest spheres, full to their 630,000 gallon capacity were saved from BLEVE by water from 100 rail tank cars. Contents of these two spheres then burned under controlled conditions.	\$22.5M
Priola, Italy (05/19/85)	Petrochemical Plant	Fire from ignition of escaped hydrocarbon caused explosion of a tall vertical propane tank, skyrocketing the top section 1,500 feet and missing a gas holder by 30 feet. The deluge water-spray system apparently was not effective under the given fire situation.	\$72.8M
Texas City, TX (05/30/78)	Refinery	Within 20 minutes of ignition of vapor cloud, five 1,000 barrel horizontal bullets, four 1,000 barrel vertical bullets, and two additional 5,000 barrel spheres failed from missile damage or BLEVEs. Pieces of these tanks fell into other units, starting more fires.	\$93M
Houston, TX (10/19/71)		Derailment of twenty tank cars led to puncture of a vinyl chloride tank. Released fuel ignited. A vinyl chloride tank car containing less than 145 tons of vinyl chloride BLEVE'd 45 minutes later, killing one and injuring 50 people. Fireball reported as 305 meters in diameter and scattered debris up to 91 meters away.	
Crescent City, IL (06/21/70)		Ten rail cars with carrying capacity of 33,000 U.S. gallons of propane apiece derailed. Propane from a punctured tank car was released and ignited causing six of the tank cars to rupture and BLEVE. Sixty-six people were injured and business section of town destroyed.	\$3M
New Jersey Turnpike, 1 mile south of exit 8 (09/21/72)		Friction sparks ignited fuel leaking from tractor-trailer fuel tank and spread to propylene leaking from cargo tank, engulfing a substantial portion of cargo tank in flame. Twenty to 25 minutes later, the cargo tank exploded, burning or otherwise injuring 28 people, one of whom was 600 feet away from the explosion. Two people trapped in an automobile wedged between the tractor-trailer and guard-rail were killed. A 27-foot long piece of the trailer tank was thrown 1307 feet northeast and 400 feet east of the explosion center.	

Sources:

Houston, TX and Crescent City, IL incidents from Lewis, David J. "Unconfined Vapour-Cloud Explosions-Historical Perspective and Predictive Method Based on Incident Records." 1980. Prog. Energy Comb. Sci., Vol. 6, pp. 151-165. Pergamon Press, Ltd.

New Jersey Turnpike incident from Eisenberg et al., Vulnerability Model: A Simulation for Assessing Damage Resulting from Marine Spills. June 1975. Prepared for Department of Transportation, U.S. Coast Guard Office of Research and Development.

Other incidents from M & M Protection Consultants, 1990.

#### 6.4 Pool Fires

A liquid pool fire is a fire involving a quantity of liquid fuel spilled on the surface of the land or water. An ignition source must start the pool fire. Primary hazards of liquid pool fires to people and property involve exposure to thermal radiation and/or toxic or corrosive products of combustion (FEMA, DOT, EPA 1989).

One incident involving a pool fire occurred at Hearne, Texas, on May 14, 1972. Rupture of an eight-inch crude oil pipeline caused the release of oil onto the surface of a nearby river. Oil on the surface of the water reportedly travelled through culverts under a highway and railroad and collected on a stock pond located 1,800 feet from the point of the rupture. After ignition of the oil vapors by an unidentified source, a fire began along the stream and burned back through the culverts and to the stock pool. Described as "1,800 feet long and several hundred feet high", the fire stopped all highway and railroad traffic. The fire was fueled by 7,913 barrels of released crude oil (Eisenberg, 1975).

#### 6.5 Jet Fires

Transportation and storage tanks or pipelines containing compressed or liquefied gases may discharge gases at a high speed if somehow punctured or ruptured during an accident. The gas discharging or venting from the hole will form a gas jet that "blows" into the atmosphere in the direction the hole is facing, all the while entraining and mixing with air. When the gas is flammable and it encounters an ignition source, a flame jet of considerable length may form. For chemicals that are liquid under ambient conditions, no gas jet will form; liquid or vapor might leak out through a puncture or break, but will not blow out.

#### 6.6 Projectiles

Projectiles resulting from BLEVEs and VCEs present potential hazards in addition to the hazards of heat radiation and blast overpressures. Projectiles can kill people, pierce chemical tanks/reactors, sever chemical and electrical pipelines, destroy fire fighting equipment, and even start fires far from the explosion. Frequently, projectiles compound an already catastrophic situation.

According to AIChE (1987), vessels that fail under pressure (e.g., in BLEVEs) generally produce a few large fragments. Possible fragmentations include cylindrical straight walls breaking into one or two metal sheets; the head and/or bottom breaking away from the cylinder section; and bolted and threaded inserts (thermocouples, pressure gauges) failing and generating missiles. According to Pineau et al. (1991), the mean weight of fragments from accidental explosions is of the order of 30 to 100 kg (70 to 220 pounds). Confined detonations, on the other hand, may form a relatively large number of primary fragments or shrapnel (AIChE 1987).

The M & M data base includes numerous examples of incidents with projectiles (Exhibit 6). In Grangemouth, United Kingdom, a 3-ton piece of a pressure separator was thrown 1,000 meters from an explosion. In addition, an incident in Feyzin, France, caused pieces of steel weighing up to 100 tons to be thrown 1.2 kilometers (three-quarters of a mile). One of these fragments landed on a pipeline and cut 40 lines. These incidents illustrate the danger of projectiles resulting from explosions involving flammable substances and the need to consider them in consequence analysis. However, consideration of potential damage from projectiles is largely site-specific and therefore is not incorporated into general consequence models such as WHAZAN. Analysis of projectile effects must include explosion pressure, rate of pressure rise, vessel shape, size and material of construction, as well as velocity, penetration, and range of fragments.



**Exhibit 6**  
**PROJECTILES FROM EXPLOSION INCIDENTS**

Facility	Type of Explosion	Projectile Weight	Projectile Distance
Geismar, LA	VCE	reactor head	425 m
Priola, Italy	fire and tank explosion	top section of a distillation column	450 m
Texas City, TX	heat decomposition	0.4 tons	900 m
Grangemouth, UK	overpressure in separator	3 tons	1,000 m
Romeoville, IL	VCE	20 tons	1,070 m
Mexico City, Mexico	BLEVE and VCE	20 tons	1,190 m
Feyzin, France	VCE, fire, and tank explosion	100 tons	1,200 m

Source: M & M Data Base, 1990

Two examples, shown in Exhibits 7 and 8, illustrate the complexity in estimating projectile effects. Exhibit 7, taken from AIChE course materials (1987), analyzes the overpressurization of an ethoxylation reactor in which a flange and a vessel fragment separate during the explosion. Note that the equation for calculating projectile distance assumes no air drag, and is thus conservative if the projectile does not have an aerodynamic shape and glides. Exhibit 8 includes an example from the Yellow Book (TNO 1980), in which a propane vessel explodes under ductile fracture. Exhibit 8 also presents the ethoxylation overpressurization example from Exhibit 7, calculated using the Yellow Book method.

Because the AIChE and Yellow Book methods are based on different assumptions and have different data requirements, a number of assumptions had to be made to carry out the Yellow Book calculations for the ethoxylation overpressurization example, as noted in Exhibit 8. For Scenario 1 (failure of a 30 pound flange), a distance of 34 meters was calculated using the AIChE method, while the Yellow Book method gave 70 meters, approximately twice the distance calculated by the AIChE method. For Scenario 2, where a 150 pound vessel fragment is removed from the reactor head by pressure energy, the AIChE method gave a distance of 1.25 kilometers, while the Yellow Book method gave a much shorter distance of 40 meters. These calculations are presented only as examples; the calculation methods have not been evaluated or compared in detail.

# Exhibit 7

## SAMPLE CALCULATIONS FOR PROJECTILES (AIChE)

### EXAMPLE--EXPLOSION FRAGMENTS

A 3000 gallon reactor used for ethoxylation operates at 70°C and 85 psig. The reactor contains 100 ft<sup>3</sup> of vapor space above the reaction mass. The reactor fails catastrophically at 400 psig (414.7 psi), 4 times the design pressure. Calculate the explosion effects from two ejected-material scenarios.

**Scenario 1.** A 30 pound blind flange on a 4 inch nozzle falls. Estimate fragment velocity (feet per second) and distance (feet).

Initial Velocity

$$v_o = 2.05 [ (PD^3) / W ]^{0.5}$$

(where:  $v_o$  = velocity (ft/s),  $P$  = internal pressure (psig),  $D$  = diameter of failed nozzle (in),  $W$  = weight of projectile (lb))

$$v_o = 2.05 [ (400)(4)^3 / 30 ]^{0.5}$$

$$v_o = \underline{60 \text{ ft/s}} \quad (18 \text{ m/s})$$

Distance

$$R = [ v_o^2 \sin^2(\alpha) ] / g$$

(where:  $R$  = radial distance (ft),  $\alpha$  = angle of projectile path (degrees),  $g$  = gravitational constant (ft/s<sup>2</sup>))

$$R = [ 60^2 \sin^2(45^\circ) ] / 32.2$$

$$R = \underline{112 \text{ ft}} \quad (34 \text{ m})$$

**Scenario 2.** A 150 pound vessel fragment with surface area of 10 ft<sup>2</sup> (total vapor space surface area = 120 ft<sup>2</sup>) is removed from the reactor head by pressure energy. Estimate fragment velocity and distance.

Total Pressure Energy is calculated using the equation:

$$E = 1.26 (V) (P_1/P_o) (T_o/T_1) RT_1 \ln(P_1/P_2)$$

(where:  $V$  = volume (ft<sup>3</sup>),  $P_o$  = standard pressure (psi),  $P_1$  = pressure of compressed gas (psi),  $P_2$  = final pressure of expanded gas (psi),  $T_o$  = standard temperature (K),  $T_1$  = temperature of compressed gas (K),  $R$  = universal gas constant (1.987 cal/g-mol-K))

$$E = 1.26 (100) (414.7/14.7) (273) (1.987) \ln(414.7/14.7) = 6,439,561 \text{ cal}$$

The AIChE method assumes 20% of total energy (KE, kinetic energy) is used to shatter the vessel. The kinetic energy fraction expended on the vessel fragment is needed (the fragment is 10 ft<sup>2</sup> of a total 120 ft<sup>2</sup> surface area).

$$KE = (6,439,561) (3.086 \text{ ft-lb/cal}) = 19,872,485 \text{ ft-lb}$$

$$KE = (19,872,485) (0.2) (10/120) = 331,208 \text{ ft-lb}$$

$$KE = (\frac{1}{2}mv_o^2)/g$$

Solve for  $v_o$ :

$$v_o = [ 2(KE)(g) / m ]^{0.5}$$

$$v_o = [ 2(331,208)(32.2) / 150 ]^{0.5} = \underline{377 \text{ ft/s}} \quad (115 \text{ m/s})$$

Distance (using same equation as in Scenario 1)

$$R = 377^2 \sin^2(45^\circ) / 32.2 = \underline{4114 \text{ ft}} \quad (1.25 \text{ km})$$

Therefore, results for Scenario 1 estimate that the 30 pound flange would be ejected at an initial velocity of 60 ft/sec, and travel a distance of 112 feet (34 meters). Scenario 2 results indicate the 10 square foot vessel fragment would initially separate at 377 ft/sec, and travel 4,114 feet (1,250 meters).

Source: AIChE Course Materials

**Exhibit 8**  
**SAMPLE CALCULATIONS FOR PROJECTILES (YELLOW BOOK)**

**EXAMPLE A-WORKED PROJECTILE**

Propane is contained in a carbon steel vessel, having 0.015 m thickness, 4 m diameter, 8 m length (100 m<sup>3</sup> volume), and weighing 15 metric tons. A 0.15 m diameter nozzle is connected to the vessel, at a height of 10 m. The vessel has an operating pressure of 2 MPa, and bursts under ductile fracture at 5 MPa. Operating temperature is 60°C. There is 10 m<sup>3</sup> of liquid and 90 m<sup>3</sup> vapor in the vessel. Other relevant properties are listed below:

<u>vapor</u>	<u>liquid</u>
$\gamma = 1.25$	$\rho_l = 600 \text{ kg/m}^3$
explosion pressure = 8 MPa	$c_p/h_v = 0.005$
	boiling point = -40°C

The nozzle separates from the vessel during the explosion. Find its initial velocity, and the distance the nozzle travels.

The following equation is used for calculating initial velocity of a fragment:

$$u_{t,0} = [(2/m) \times (F/(1+\epsilon^{3\gamma-3})) \times (\Delta p/(\gamma-1) \times (\pi/4) \times d^2 h)]^{0.5}$$

(where:  $u_{t,0}$  = initial velocity (m/sec),  $m$  = mass of vessel (kg),  $F$  = yield factor for fragment energy (0.6 for ductile fracture, 0.2 for brittle),  $\epsilon$  = fraction of strain of the vessel material on fracture (0.38 for carbon steels),  $\Delta p$  = change in pressure (Pa),  $\gamma$  = ratio of specific heats at constant pressure and constant volume (gases),  $d$  = diameter of cylindrical vessel (m),  $h$  = height of vapor space above any liquid present (m))

$$u_{t,0} = [(2/15000) \times (0.6/(1+0.38^{3(1.25-3)})) \times (3 \times 10^6/(1.25-1) \times (\pi/4) \times 4^2 \times 5)]^{0.5}$$

$$u_{t,0} = \underline{260 \text{ m/s}}$$

Maximum distance the projectile travels is found by iteratively solving this equation for  $r$ :

$$r_{\max} = 0.23 \times h'^{0.5} \times u_{t,0} [\exp(-C_w \times (A_f/m_f) \times \rho_a \times r)]$$

(where:  $r_{\max}$  = maximum distance from center of vessel (m),  $h'$  = ejection height (m),  $u_{t,0}$  = initial velocity (m/sec),  $C_w$  = coefficient of resistance,  $A_f$  = area of fragment (m<sup>2</sup>),  $m_f$  = mass of fragment projectile (kg),  $\rho_a$  = density of air (kg/m<sup>3</sup>),  $r$  = distance from center of vessel (m))

By substituting the equations for nozzle area for  $A_f$ , and nozzle volume multiplied by vessel material density for  $m_f$ , the ratio  $A_f/m_f$  can be simplified to  $8.55 \times 10^{-4}/d$ .

$$r_{\max} = 0.23 \times 10^{0.5} \times 260 [\exp(-1.11 \times (8.55 \times 10^{-4} / 0.15) \times 1.29 \times r)]$$

By iteratively choosing values of  $r$ , a value of  $r$  is found for which the equation is true:

$$r_{\max} = r = \underline{90 \text{ m}}$$

The nozzle travels about 90 m from the vessel.

Source: Yellow Book, Bureau for Industrial Safety (TNO), The Netherlands

# **Exhibit 8 (continued)** **SAMPLE CALCULATIONS FOR PROJECTILES (YELLOW BOOK)**

## **EXAMPLE B-CALCULATING SCENARIOS 1 & 2 FROM EXHIBIT 7 BY YELLOW BOOK METHOD**

Using this Yellow Book Method, we will now calculate Scenarios 1 and 2 from Exhibit 7 to provide a comparison of the results obtained by each method. Since the Yellow Book method is dependent on the size and shape of the rupturing container, we will first calculate the reactor size and total weight for a reactor with a capacity of 3,000 gallons or approximately 11.36 m<sup>3</sup> of space. Assuming the reactor height = 1.5(diameter of the reactor), the appropriate reactor dimensions would be a height (h') = 4.02m and diameter = 2.68m. Since there is 100 ft<sup>3</sup> of vapor space above the liquid in the vessel, the height of vapor above the liquid is h = 1.004 m. Assume the reactor is constructed of carbon steel and that the fracture is ductile F=0.6. The weight of the entire reactor can now be calculated by multiplying the total surface area of the reactor by 150 lbs/10 ft<sup>2</sup> (based on the vessel fragment described in Scenario 2.) The weight of the entire reactor is then 6373 lbs or 2891 kgs.

The ratio of specific heats (γ) for ethylene oxide is 1.21 @ 293 K. The P<sub>burst</sub> given was 414.7 psi or (4 x design capacity), therefore P<sub>explosion</sub> is assumed to be (10 x design capacity) per Yellow Book for worst case scenario or 1036.8 psi, and ΔP (P<sub>explosion</sub>-P<sub>burst</sub>) is 4.29 x 10<sup>6</sup> Pa. Assume C<sub>w</sub> = 1.11 for both Scenarios 1 and 2.

Since the Yellow Book calculation of u<sub>t,o</sub> is based on the vessel from which the projectile originated and is independent of the actual projectile which is ejected, the initial velocity calculation of u<sub>t,o</sub> is identical for the flange in Scenario 1 and the reactor fragment in Scenario 2. The initial speed of both the flange and the reactor fragment can be calculated:

$$u_{t,o} = [(2/2891) \times (0.6/(1+0.38^{3(1.21)-3})) \times (4.29 \times 10^6 / (1.21-1)) \times (\pi/4) \times 2.68^2 \times 1.004]^{0.5}$$

$$u_{t,o} = 197 \text{ m/s.}$$

The Yellow Book method is specific to the size and shape of the ejected object only when the deceleration term is added in the calculation of r<sub>max</sub>. The maximum distance the projectile travels is found by iteratively solving this equation for r:

$$r_{max} = 0.23 \times h^{0.5} \times u_{t,o} [\exp (-C_w \times (A_f/m_f) \times \rho_a \times r)].$$

**Scenario 1** Assuming the flange has a diameter of 8" or 0.2032m (2 x the nozzle diameter), the surface area of the flange (A<sub>f</sub>) can be calculated as 0.0324 m. The mass of the flange (m<sub>f</sub>) was given in Scenario 1 as 30 lbs or 13.61 kg. Finally, assuming C<sub>w</sub>=1.11, r<sub>max</sub> can be calculated:

$$r_{max} = 0.23 \times 4.02^{0.5} \times 197 [\exp (-1.11 \times (0.0324 / 13.61) \times 1.29 \times r)].$$

By iteratively choosing values of r, a value of r is found for which the equation is true:

$$\text{Maximum distance travelled by the flange } r_{max} = r = 70 \text{ m.}$$

**Scenario 2** The area of the vessel fragment (A<sub>f</sub>) is given in Scenario 2 as 10 ft<sup>2</sup> or 0.929 m<sup>2</sup>. The mass (m<sub>f</sub>) of the vessel fragment was also given in Scenario 2 as 150 lbs or 68.04 kg. Finally, assuming C<sub>w</sub>=1.11, r<sub>max</sub> can be calculated:

$$r_{max} = 0.23 \times 4.02^{0.5} \times 197 [\exp (-1.11 \times (0.929 / 68.04) \times 1.29 \times r)].$$

By iteratively choosing values of r, a value of r is found for which the equation is true:

$$\text{Maximum distance travelled by the reactor fragment } r_{max} = r = 40 \text{ m.}$$

## 7.0 Accident Factors and Model Inputs for Consequence Analysis

Accident scenario factors (e.g., concentration, confinement, release pressure) could have an effect on the severity of the consequences of an accident involving a flammable chemical. A few factors such as quantity released, temperature/pressure conditions, and atmospheric stability are common inputs to most consequence models. However, most models are limited in the number of factors that can be input into the consequence analysis. It is impossible to list all of these factors, especially those that are site-specific (e.g., characteristics of terrain and local micrometeorological effects such as slight wind shifts). The effect of these factors on the consequences of flammable chemical accidents is difficult to measure, however, this section will qualitatively evaluate this effect. Later in this section, the factors and modeling inputs that can be incorporated into the models will be discussed.

### 7.1 Model Inputs

The WHAZAN model (discussed in Section 5.1 and in Appendix B, Section B.1) was applied to flammable liquids and gases to determine the distance that might be affected for various types of accidents, using varying quantities released and various hazard criteria levels. WHAZAN is not sufficiently complex to incorporate certain accident factors such as flashback and projectiles for vapor cloud explosions. However, several WHAZAN model inputs that will help determine accident consequences include the following:

- Specific physical/chemical properties of the chemical involved (e.g., volatility and heat of combustion);
- The quantity of the chemical involved;
- The type of release (instantaneous or prolonged);
- The initial conditions (temperature and pressure) of the chemical just prior to release;
- Meteorology (particularly when modeling scenarios that involve dispersion); and
- The surface roughness over which the release passes.

These factors and their relationship to consequence modeling are discussed below.

#### 7.1.1 Chemicals and Quantities Chosen for Modeling

A variety of chemicals were modeled for selected quantities. Ten common hydrocarbons, including alkanes, alkenes, and aromatics, of widely varying volatility (boiling points from -103°C to 137°C) and flammability (as indicated by flash point) were chosen for consequence modeling as representative examples of a range of flammable chemicals that may be found in commerce in high volumes. Volatility and flammability are important characteristics in determining accident consequences. The selected chemicals included ethylene, propane, propylene, n-butane, pentane, hexane, heptane, toluene, p-xylene, and gasoline. Physical/chemical properties of these chemicals are listed in Exhibit E-2, Appendix E. Ethylene, propane, propylene, and n-butane are gases under ambient conditions; the other chemicals are liquids. WHAZAN modeling was carried out for releases of 1,000, 2,500, 5,000, 7,500, 10,000, 25,000, 50,000, 100,000 and 180,000 pounds of each of the ten hydrocarbons to gain insight into the impact of the size of an accidental release on potential consequences. Results of modeling are presented in Section 8.

Modeling of 100,000 pound releases of each of the ten hydrocarbons was carried out using the other methods discussed in Section 5 to compare the results from other models (PC-based calculation methods

and others) with WHAZAN. The methods for all the models used are discussed in Appendix B. Results of modeling by all methods were found to be in reasonable agreement. Eight other organic chemicals, including ethylene oxide, ethyl chloride, acetaldehyde, acetone, trichloroethylene, acetic acid, benzaldehyde, and dimethyl sulfoxide were also modeled for 100,000 pound releases using the WHAZAN model for comparison with the hydrocarbons. Some of these chemicals (e.g., trichloroethylene and dimethyl sulfoxide) are not considered very flammable; they were included for comparison purposes. Results of modeling 100,000 pound releases of the hydrocarbons by all methods and WHAZAN results for the additional chemicals are presented in Exhibit D-1, Appendix D.

### **7.1.2 Instantaneous and Prolonged Releases**

Instantaneous releases are those that take place over a period of time ranging from a few seconds to several minutes and then essentially stop. The result of such a release typically is a liquid pool, a puff of vapor or gas, or distinct cloud, but can also involve an explosion. A sudden catastrophic vessel failure or the failure of a large piping connection can be considered examples of instantaneous releases. Instantaneous releases were considered likely to have potentially more severe consequences than prolonged releases (see below) and were assumed as the type of release in the comparative modeling using all methods.

Prolonged or continuous releases take place over longer periods of time and, when atmospheric dispersion is involved, typically produce plumes stretched out over longer distances. Failure of a small piping connection or of a piping gasket are examples of potential prolonged releases. For modeling purposes, prolonged releases were assumed to emanate from 1.5 inch diameter holes in containment vessels. This simulates the shearing off of a small instrument connection on a vessel or a gasket leak in a larger piece of piping. Prolonged releases were modeled using WHAZAN for comparison with instantaneous releases; the consequences are, in general, smaller.

### **7.1.3 Initial Conditions Prior to Release**

Flammable chemicals are handled and/or stored at a wide variety of temperatures and pressures at industrial facilities. Conditions can range from extremely severe processing conditions (high temperature and pressure) to relatively low severity storage conditions. Very volatile chemicals may be stored as liquids under pressure and/or at low temperatures. Less volatile chemicals can be stored at ambient temperatures and pressures. Accident consequence modeling is dependent on initial release conditions. Because it is not uncommon for storage vessels to be sited closer to plant fencelines and hence neighboring communities than processing equipment, and because storage vessels generally contain much larger volumes of material than processing equipment, storage temperatures and pressures that may be found in industry practice were assumed as initial release conditions for modeling purposes. Temperatures and pressures used in modeling are listed by chemical in Exhibit E-1, Appendix E.

### **7.1.4 Meteorology**

The primary meteorological conditions used for modeling by all methods were 3.0 meters per second wind speed and D atmospheric stability, representing average or neutral atmospheric conditions rather than worst case situations. More extreme conditions (for dispersion) of 1.5 meters per second wind speed and F atmospheric stability were also used for WHAZAN modeling to show the effect of varying meteorological conditions on accident consequences. As explained in the Green Book (EPA, FEMA, DOT 1987), these conditions correspond to stable air and low wind speed, conditions under which dispersion results for distances to various hazard criteria levels are generally larger than those calculated under conditions usually considered typical.

### 7.1.5 Surface Roughness

Surface roughness influences the dispersion and gravity spreading of dense gas clouds. It is a measure of the irregularity of the terrain over which a cloud passes. Irregularities include mountains, trees, flat rural areas, and city buildings. The size of the surface feature relates to the size of a surface roughness factor (e.g., large irregularities are assigned large factors). The surface roughness factor of 0.1 meters is the WHAZAN model default value that is consistent with long grass conditions.

## 8.0 Hazard Criteria

The extent and severity of the impacts of an accident depends on the type of consequence that results. Accidents involving flammable substances can result in thermal radiation from fires or blast overpressures from explosions, or both. The consequences for various types of accidents have been summarized below:

<u>Accident</u>	<u>Consequence</u>	<u>Units</u>
Vapor Cloud Explosion	Overpressure	psi
BLEVE	Thermal radiation, duration of exposure	kW/m <sup>2</sup> , seconds
Pool Fire	Thermal radiation, duration of exposure	kW/m <sup>2</sup> , seconds
Jet Fire	Thermal radiation, duration of exposure	kW/m <sup>2</sup> , seconds
Vapor Cloud Fire	Ignition of fire	LFL

where psi = pounds per square inch, kW/m<sup>2</sup> = kilowatts per square meter, and LFL = lower flammable limit; these are discussed further below.

For modeling purposes, several hazard criteria levels of overpressure, thermal radiation, or concentration associated with each type of accident consequence were used for modeling. The effects of the hazard criteria and the distances resulting from modeling can then be used by EPA in regulatory determinations. For a given accident, the WHAZAN model was used to calculate the distance from the accident site to the chosen hazard criteria level. The hazard criteria levels that were used in modeling may have effects that range from minor injury to humans through various levels of property damage to potentially lethal effects on humans (see Appendix C). These are discussed below by type of accident.

### 8.1 Hazard Criteria for Vapor Cloud Explosions

The consequence of greatest concern for vapor cloud explosions is the blast wave. Blast waves from accidental explosions can cause damage to people and property by subjecting them to transient crushing pressures and winds. Relatively simple concepts have been used to correlate blast wave properties with damage. Blast wave damage is primarily a function of either the peak overpressure, the impulse, or some combination of these factors. Peak overpressure is most commonly used. For modeling vapor cloud explosions, overpressures of 0.3, 0.5, 1.0, 3.0, and 10.0 psi were considered. At an overpressure of 0.3 psi, 10 percent of window glass may be broken (Lees 1980). An overpressure level of 0.5 psi can cause windows to shatter, with some frame damages (Brasie and Simpson 1968). Overpressure of 1.0 psi can cause partial demolition of houses and is the threshold for skin laceration from flying glass (Lees 1980). An overpressure level of 3.0 psi can cause steel frame buildings to become distorted and pulled away from their foundations (Lees 1980); this overpressure can also hurl a person to the ground (Brasie and Simpson 1968). An overpressure of 10 psi may totally destroy buildings (Lees 1980) and is the threshold for lung hemorrhage (U.S. DOT 1988). Pineau et al. (1991) suggest overpressure levels of 170 mbar (2.5 psi) as the threshold for significant lethality and 50 mbar (0.7 psi) as the upper limit for reversible effects on humans, based on a review of accidents in France. Appendix C, Section C.1.1,

presents additional information on damage and injury caused by various overpressure levels from explosions.

## **8.2 Hazard Criteria for Vapor Cloud Fires**

The minimum concentration of a vapor or gas in air that will ignite and propagate flame is known as its lower flammable limit (LFL) concentration or lower explosive limit (LEL) concentration. The words flammable and explosive are used interchangeably such that LFL values equal LEL values; the concentration of a fuel that will burn in air also can be expected to explode under the appropriate conditions. Similarly, the maximum concentration of a gas or vapor in air that will ignite and propagate flame is known as the upper flammable limit (UFL) or upper explosive limit (UEL) of the fuel (FEMA, DOT, EPA 1989).

For vapor cloud fires, dispersion modeling was carried out using concentrations equal to 50 percent of the LFL, the LFL, and twice the LFL. Levels below the LFL are used to account for variability within the cloud from its edge to its center and inaccuracies in dispersion modeling. This is based on guidance in the WHAZAN manual (WHAZAN 1988) which recommends the following:

When calculating safe distances from flammable releases, these difficulties [uncertainties in concentration] indicate that the analyst should consider concentrations somewhat below the LFL. A concentration of LFL/2 or LFL/4 is normally used.

## **8.3 Hazard Criteria for BLEVEs, Pool Fires, and Jet Fires**

The consequence of greatest concern resulting from BLEVEs, pool fires, and jet fires is heat radiation. In the case of BLEVEs, injuries and fatalities might also result from overpressures and container fragment projectiles, but thermal radiation is considered to be the consequence of greatest concern and is the consequence addressed in the modeling. Human injury or fatality from heat radiation from fires is likely to occur as a result of direct exposure to a fire rather than as a result of property damage caused by a fire. The extent of the injury caused by heat radiation depends both on the heat level and the time of exposure. The duration of the fire and the length of time it might take an exposed person to escape or take shelter from the fire would be important considerations.

The WHAZAN model produces results for duration of the fire and distance from the fire for three heat radiation levels for BLEVEs, pool fires, and jet fires. For BLEVEs and jet fires, duration and distance results are produced for heat radiation levels of 4.0, 12.5, and 37.5 kW/m<sup>2</sup>. According to the WHAZAN manual, a heat radiation level of 4.0 kW/m<sup>2</sup> would lead to a 1 percent probability of fatality after an exposure time of 150 seconds. For 12.5 kW/m<sup>2</sup> the probability of fatality is 1 percent after a 30 second exposure and 50 percent after an exposure time of 80 seconds. For a heat radiation level of 37.5 kW/m<sup>2</sup> the probability of fatality is 1 percent for an 8-second exposure, 50 percent for a 20-second exposure, and 99 percent for a 50-second exposure (WHAZAN 1988). For pool fires, WHAZAN gives results for 1.6, 4.0, and 12.5 kW/m<sup>2</sup>. A heat radiation level of 1.6 kW/m<sup>2</sup> would lead to a 1 percent probability of fatality after 500 seconds (WHAZAN 1988).

Pineau et al. suggest heat radiation thresholds of 5.2 kW/m<sup>2</sup> for severe casualties and lethality and 2.9 kW/m<sup>2</sup> as the upper limit for reversible radiation effects for a fire lasting 60 seconds or more. These thresholds are intended to apply when escape from the heat effects is not possible. Pineau's threshold levels seem consistent with the heat radiation information presented in the WHAZAN manual. Appendix C, Section C.3.1, presents additional information on thermal radiation.



## 9.0 Modeling Results

WHAZAN modeling was carried out for vapor cloud explosions, vapor cloud fires, BLEVES, pool fires, and jet fires of the hydrocarbons using the assumptions discussed above. For vapor cloud explosions, data from actual events described in the M & M data base were compared with results predicted by WHAZAN. All WHAZAN results are presented in the following sections by consequence type. Resulting distances for selected quantities and several hazard criteria levels are provided. Results of modeling by other methods and additional WHAZAN results are presented in Exhibit D-1, Appendix D. The inputs used for the WHAZAN model are presented in detail in Appendix E; Appendix E also lists inputs for the ARCHIE model. As noted earlier, results from all the methods are in reasonable agreement.

### 9.1 Vapor Cloud Explosion Results

#### 9.1.1 Modeling Results for Four Hydrocarbons

WHAZAN Model Used. To obtain the WHAZAN modeling results presented here, the linked models were used only to determine the fraction of pressurized or refrigerated gas instantly flashed to vapor (the model calculates fraction flashed only for substances that are gases under ambient conditions). The fraction flashed was used to estimate the flammable mass in the cloud; this quantity was used to run the stand-alone model for vapor cloud explosion, rather than the linked models. The linked models were not used for vapor cloud explosions because it was found that these models did not produce reasonable results for this type of consequence; i.e., the quantity apparently assumed to be in the cloud seemed unreasonably high (much higher than the quantity that would be immediately flashed into vapor).

Quantity in Cloud. For modeling purposes, the quantity in the cloud was assumed to be the fraction flashed. According to Kletz (1977), the adiabatic flash gives an estimate of the minimum amount of material present in the cloud. Some material is likely to be released into the cloud as aerosol, but WHAZAN does not provide a method for estimating aerosolization. The entire quantity in the cloud was assumed to be within the explosive limits. In an actual incident, the quantity in the cloud might be greater than the fraction flashed, and the quantity within the explosive limits might be smaller than the total quantity in the cloud because of dispersion. The most conservative assumption would be to assume the entire quantity is in the cloud; such an occurrence seems very unlikely, however.

Yield Factor. The explosive yield factor was assumed to be 0.11, the default value for WHAZAN (i.e., 11 percent of the quantity in the cloud was assumed to participate in the explosion). This is intended to be a conservative assumption. The actual explosive yield in a vapor cloud explosion may vary greatly, depending on the substance involved, storage and release conditions, and other factors. According to Lees (1980), yield factors are usually between one and 10 percent; however, cases of much higher efficiencies have been reported (e.g., 25 to 30 percent in one incident) (Lees 1980).

Overpressure Levels. WHAZAN results for vapor cloud explosions are presented as distances to four characteristic damage levels; overpressures related to these damage levels are not presented but have been estimated for this report. Affected distances calculated by WHAZAN appear to be based on the scaling law of distances, which states that distance is proportional to the cube root of quantity of explosive material. For TNT, empirical graphs of scaled distance versus overpressure have been derived. The WHAZAN distances are based on "limit values" related to damage levels. It was assumed, based on the scaling law, that the WHAZAN distances would be proportional to the scaled distance values for TNT as presented in Lees (1980), the source cited in the WHAZAN manual. Using this relationship and the descriptions of the damage levels in the WHAZAN manual, the Yellow Book, and Lees, the overpressure related to each limit value was estimated.

Results. Exhibit 9 presents WHAZAN modeling results for vapor cloud explosions of four hydrocarbon gases for quantities of 1,000 to 180,000 pounds. Ethylene and propane are assumed to be liquefied by refrigeration; propylene and n-butane are assumed to be liquefied under pressure. Vapor cloud explosion results could not be obtained for liquids under ambient conditions. The exhibit shows the fraction flashed, obtained from the linked models, and the quantity assumed to be in the cloud, calculated from the total quantity released and the fraction flashed. Distances calculated for several overpressure levels are presented. Although the modeling shows distances of approximately 100 meters for release quantities as small as about 5,000 pounds at overpressures of 1.0 psi and lower, the probability of a vapor cloud explosion occurring is relatively low for vapor clouds containing quantities smaller than 10,000 pounds (API 1990, Prugh 1987), as noted earlier. Note also that the quantity in the cloud is considerably smaller than the quantity released; i.e., a release of 10,000 pounds of flammable material would probably result in a cloud containing much less than 10,000 pounds (Exhibit 9 shows 150 to 3,300 pounds in the cloud for a release of 10,000 pounds). Distances for ethylene and propane, assumed to be liquefied by refrigeration, are considerably shorter than for propylene and n-butane, assumed to be liquefied under pressure, probably because at reduced temperatures less of the ethylene and propane are in the vapor phase to contribute to the amount flashed upon release. For propylene and n-butane, modeling results indicate distances greater than 100 meters for an overpressure of 1.0 psi for all the quantities modeled. For an overpressure of 1.0 psi, distances for propane range from 49 meters for a 1,000 pound release to 276 meters for a 180,000 pound release, while for propylene the distances are from 139 meters for 1,000 pounds to 787 meters for 180,000 pounds.

Exhibit 9 shows results for ethylene and propane under low-temperature storage conditions. Ethylene and propane were also modeled assuming initial release conditions of higher temperatures and pressures, similar to the conditions assumed for propylene and n-butane; under these conditions, distances were similar to those found for propylene and n-butane, indicating that gases liquefied by refrigeration may pose less potential risk of vapor cloud explosion than gases liquefied under pressure.

Exhibit 10 shows WHAZAN modeling results as a graph of quantity released versus distance for vapor cloud explosions, based on 1.0 psi overpressure. It is assumed that graphs of quantity versus distance for other overpressure levels would show similar increases in distance with increasing quantity released. Quantities released displayed on the graph range from 1,000 to 50,000 pounds. The curves shown in Exhibit 10 illustrate the fact that distance is proportional to the cube root of the quantity of explosive, according to the scaling law of distances, which is the basis for WHAZAN modeling of vapor cloud explosions. Thus, at a specific hazard criteria level, the smaller the quantity released, the much smaller the distance for experiencing the impact.

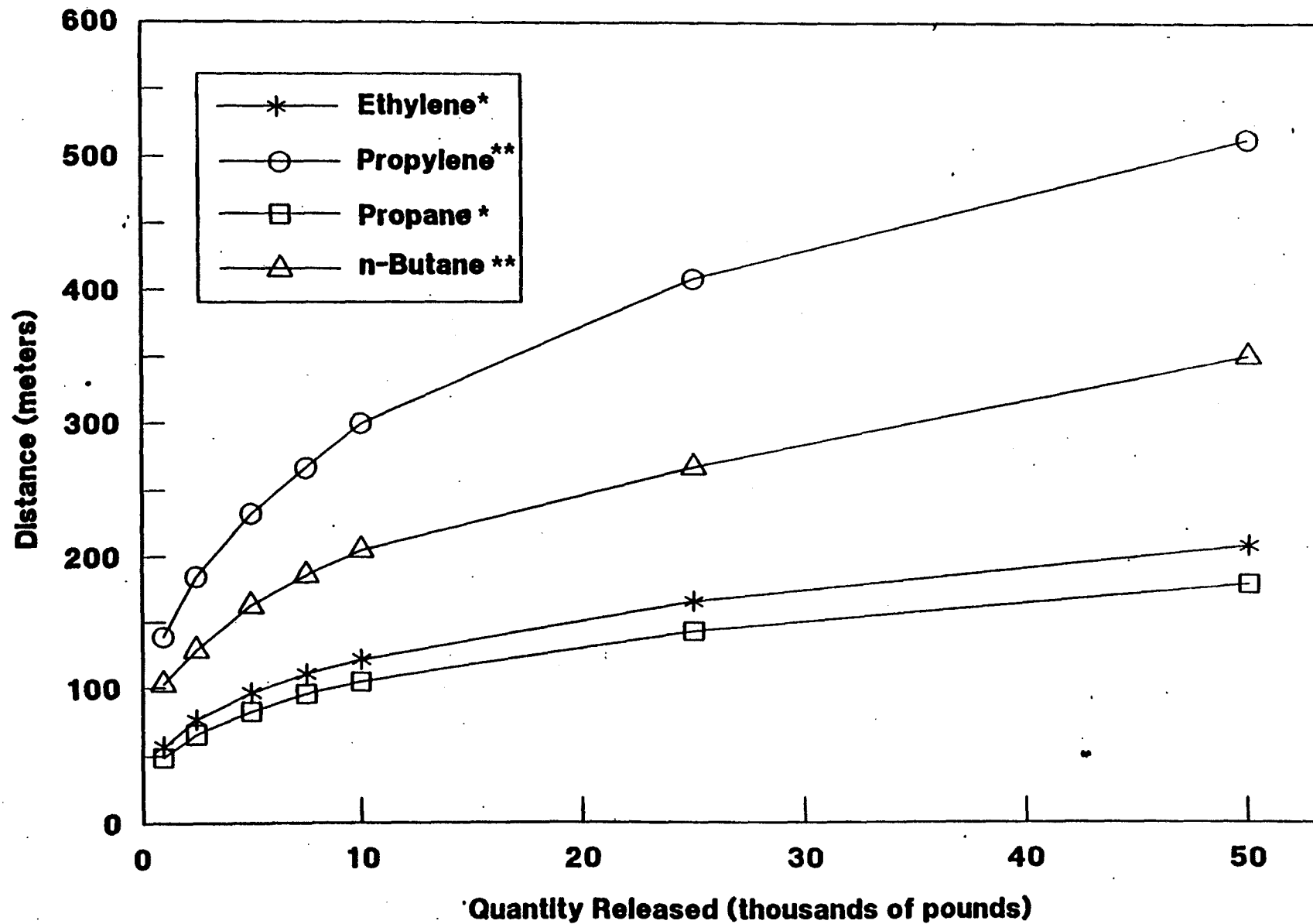
Exhibit C-6, in Section C.1.2 of Appendix C, shows WHAZAN modeling results for releases of 100,000 pounds of ethylene and propylene. Distances to different overpressure levels are displayed graphically. These results indicate that the choice of overpressure level has a significant effect on determining the affected distance, particularly at low overpressures. For example, for propylene the affected distance decreases from 1,121 meters to 647 meters if an overpressure of 1.0 psi is used rather than 0.5 psi. Similar decreases occur for the other chemicals. The graph of distance versus overpressure becomes relatively flat between overpressures of 3.0 and 10.0.

**Exhibit 9**  
**DISTANCES FOR VAPOR CLOUD EXPLOSIONS OF FOUR LIQUEFIED GASES**  
**FOR INSTANTANEOUS RELEASES OF 1,000 TO 180,000 POUNDS**  
**DETERMINED USING FRACTION FLASHED, WHAZAN STAND-ALONE MODEL**

Chemical (Initial Conditions)	Quantity Released (pounds)	Fraction Flashed	Quantity in Cloud (pounds)	Distance in Meters to the Following Overpressures				
				0.3 psi	0.5 psi	1.0 psi	3.0 psi	10.0 psi
Ethylene (liquefied by refrigeration 175 K, 1.3 Bars)	1,000	0.023	23	151	98	57	23	11
	2,500		58	205	134	77	31	15
	5,000		115	259	168	97	39	19
	7,500		173	296	193	111	44	22
	10,000		230	326	212	122	49	24
	25,000		575	443	288	166	66	33
	50,000		1,150	558	362	209	84	42
	100,000		2,300	703	457	263	105	53
	180,000		4,140	855	556	321	128	64
Propylene (liquefied under pressure 293 K, 13.3 Bars)	1,000	0.329	329	372	242	139	56	28
	2,500		823	494	321	185	74	37
	5,000		1,645	622	404	233	93	47
	7,500		2,468	712	463	267	107	53
	10,000		3,290	801	521	300	120	60
	25,000		8,225	1,090	706	408	163	82
	50,000		16,450	1,370	890	513	206	103
	100,000		32,900	1,730	1,121	647	259	129
	180,000		59,220	2,100	1,364	787	315	157
Propane (liquefied by refrigeration 232 K, 1.3 Bars)	1,000	0.015	15	130	85	49	20	10
	2,500		38	177	115	66	26	13
	5,000		75	223	145	83	33	17
	7,500		113	255	166	96	38	19
	10,000		150	280	182	105	42	21
	25,000		375	381	247	143	57	29
	50,000		750	479	312	180	72	36
	100,000		1,500	604	393	227	91	45
	180,000		2,700	735	478	276	110	55
n-Butane (liquefied under pressure 293 K, 6.3 Bars)	1,000	0.113	113	275	179	103	41	21
	2,500		283	345	224	129	52	26
	5,000		565	434	282	163	65	33
	7,500		848	497	323	186	75	37
	10,000		1,130	546	355	205	82	41
	25,000		2,825	713	463	267	107	53
	50,000		5,650	936	607	350	140	70
	100,000		11,300	1,180	766	442	177	88
	180,000		20,340	1,430	933	538	215	108

Exhibit 10  
QUANTITY RELEASED VERSUS DISTANCE  
FOR VAPOR CLOUD EXPLOSIONS, INSTANTANEOUS RELEASES

WIAZAN Modeling for 1,000-50,000 pounds, 1.0 psi Overpressure



\* Liquefied by refrigeration  
\*\* Liquefied under pressure

Issues. Several factors used in WHAZAN to model the consequences of a vapor cloud explosion may vary widely in an actual event; therefore, the results of an actual incident may differ from the results presented here. The modeling could have been carried out using more or less conservative assumptions, and larger or smaller results would have been obtained. For this modeling, a conservative yield factor of 11% was used; generally, yields are likely to be lower, but higher yields have also been reported. Use of the fraction flashed as the quantity in the cloud is not a conservative assumption, because additional material is likely to be carried into the cloud. Assuming the entire cloud is within the explosive range is conservative, however.

#### **9.1.2 Modeling Using Other Meteorological Conditions**

WHAZAN modeling was also carried out using meteorological conditions of 1.5 meters per second wind speed and F atmospheric stability. This was done to show the impacts of varying meteorological conditions on accident consequences. Results for vapor cloud explosions were identical to those obtained using 3.0 meters per second wind speed and D atmospheric stability, indicating that the vapor cloud explosion results using WHAZAN are not dependent on meteorological assumptions made. These results are presented in Exhibit D-1, Appendix D.

#### **9.1.3 Modeling Prolonged Releases**

WHAZAN modeling for a prolonged release was also undertaken to compare the results of assuming an instantaneous versus a prolonged release. However, this attempt, which used moderate meteorological conditions, produced no vapor cloud explosion results. It was not possible to determine why the model produced no vapor cloud explosion data for prolonged releases. ARCHIE modeling was then tried for modeling prolonged releases (assuming a 1.5-inch hole) of 1,000 to 10,000 pounds of propylene. In the case of a liquid release, the results for both instantaneous and prolonged releases were essentially identical; therefore, these results are not presented here. If a prolonged gas release was assumed, the model calculated the same distances for each different quantity released. Releases of other gases would probably provide similar results. These results are not logically consistent and the particular reason(s) for the inconsistencies are not known. However, this may be a function of the limitations of the ARCHIE model at small release quantities. As discussed earlier, vapor cloud explosions are more likely if ignition occurs within one minute of a release (Wiekema 1984); under these circumstances, prolonged release models are not appropriate.

### **9.2 Comparison of Vapor Cloud Explosion Data and WHAZAN Results**

To verify the general assumptions used and the results obtained from the vapor explosion algorithms contained in WHAZAN, actual vapor cloud incidents were modeled by the WHAZAN Stand Alone Model. The M & M data base provided the information on vapor cloud incidents (e.g., chemical, quantity released) which formed the basis of the model inputs. Similar to the previous analysis, the WHAZAN default value for explosion yield of 11 percent was used. Five vapor cloud explosion incidents involving four different chemicals were studied. Exhibit 11 compares the overpressure and distance results from the WHAZAN model with the overpressures and distances calculated or measured in the actual explosions. Overpressures for the incidents modeled are reported in the M & M data base or were estimated based on the descriptions of damage. The greatest distance at which glass was broken was assumed to occur at 0.3 psi. In the modeling, the use of fraction flashed was not necessary because the accident description already provided an estimate of the quantity in the cloud rather than the quantity released. The five vapor cloud explosions are described further following Exhibit 11.

**Exhibit 11  
COMPARISON OF EXPLOSION DATA AND WHAZAN RESULTS**

Incident	Chemical (Initial Conditions)	Quantity Released into Cloud (pounds)	WHAZAN RESULTS (Distance in Meters to the Following Overpressures)				EXPLOSION DATA (Based on Reported Damage)
			0.3 psi	1.0 psi	3.0 psi	10.0 psi	
Case #1: (Pasadena)	Ethylene 700 psi	85,000	2340	878	351	175	7 psi at 100 meters
Case #2: (Norco)	Propane 270 psi and 130° F	20,000	1430	537	215	107	as high as 10 psi near epicenter (within 100 meters)
Case #3: (East St. Louis)	Propylene	107,000	2500	938	375	188	0.15 - 0.4 psi at 1000 meters
Case #4: (Port Hudson)	Liquified Propane 942 psig	132,000	2690	1010	403	202	0.3 psi at 8000 meters
Case #5: (Flixborough, UK)	Cyclohexane 155° C	60,000	2020	757	303	152	10 psi at 135 meters 3 psi at 335 to 535 meters; 0.3 psi at 2400 meters

\* Based on estimated TNT equivalence of 10 tons

Notes: 0.3 psi is assumed to be overpressure level for glass breakage.

Explosion yield factor of 11% is assumed for above cases.

Atmospheric conditions are not needed as input to WHAZAN Stand Alone Model.

Case #1 Comparison In one accident in Pasadena, Texas, 85,000 pounds of a mixture containing primarily ethylene was released through a valve at 700 psi. The vapor cloud ignited after approximately 1 minute. The blast was equivalent to the detonation of 10 tons of TNT, or approximately 7 psi overpressure at 100 meters. A run of the WHAZAN model with similar inputs gave a range of overpressures and distances (e.g., 10 psi overpressure at 175 meters and 3 psi overpressure at 351 meters). The explosion data was just outside this predicted range. Due the exponential relationship between the overpressure and distance, this difference between the WHAZAN results and the explosion data may not be significant.

Case #2 Comparison In a refinery vapor cloud explosion in Norco, Louisiana, 20,000 pounds of propane were released through a failed pipe at 270 psi and 130° F. A vapor cloud formed during the 30 seconds between failure and ignition. The resulting explosion of propane caused overpressures as high as 10 psi within 100 meters. The 10 psi overpressure was reported in the M

& M data base (1990) based on analysis of facility equipment in the blast path. Using the WHAZAN model, an overpressure of 10 psi at 107 meters was predicted.

Case #3 Comparison Rail cars collided in East St. Louis, Illinois releasing 107,000 pounds of propylene. An elongated cloud covering about 5 acres was formed before an ignition source ignited the cloud after about a 5 minute delay. The resulting vapor cloud explosion caused an overpressure of between 0.15 and 0.4 psi at 1 kilometer from the explosion center. At this distance, a school suffered extensive interior damage. A run of the WHAZAN model with similar inputs gave 0.3 psi at 2.5 kilometers.

Case #4 Comparison In Port Hudson, Missouri, a pipeline ruptured and released 132,000 pounds of liquefied propane at 942 psig into a cloud. A vapor cloud, covering about 10 acres, was ignited after 24 minutes. The resulting explosion broke windows 8 kilometers away; overpressure for window breakage was assumed to be 0.3 psi. A run of the WHAZAN model with similar inputs gave 0.3 psi at only 2.7 kilometers.

Case #5 Comparison In a petrochemical plant in Flixborough, United Kingdom, a massive failure of a 20-inch diameter bypass assembly released approximately 60,000 pounds of primarily cyclohexane at 155° C. The huge vapor cloud, measuring 120 by 150 meters, was ignited. The resulting explosion and fire destroyed much of the plant. At 120 meters from the center of the explosion, the walls of a brick building collapsed. The vapor cloud explosion at Flixborough has been studied extensively and therefore has much damage data (Sadee 1977). The overpressure was between approximately 10 psi at 135 meters, 3 psi at 335 to 535 meters, and approximately 0.3 psi (between 10 and 20 percent of windows were damaged) at 2,400 meters away. A run of the WHAZAN model with similar inputs gave comparable results with 10 psi at 152 meters, 3 psi at about 300 meters, and 0.3 psi at about 2000 meters.

Exhibit 11 shows that the WHAZAN model results for cases #1, #2, #3, and #5 generally correlate with the consequences of a vapor cloud explosions. The correlations in cases #3 and #5 are stronger than cases #1 and #2 because overpressures at distances further from the explosion center are more easy to predict and measure than distances closer to the explosion center. However, in three of these cases, WHAZAN results were consistently more conservative than the explosion data (at same overpressure, predicted distances using WHAZAN are greater than distances measured in actual explosions).

The generally conservative WHAZAN results in cases #1, #2, and #3 may be due to the potentially conservative assumption of 11 percent explosive yield. An explosive yield factor of 2 percent was mentioned as a reasonable estimate by several members of EPA's Science Advisory Board on flammable chemicals. The 2 percent explosion yield factor produces results which more closely simulate the explosion data. However, the 11 percent factor used to calculate vapor cloud explosion results in Section 9.1 is acceptable because for this analysis, conservative estimates of affected distances is desired.

In case #4, the WHAZAN results seem to underestimate the consequences significantly. However, this vapor cloud explosion was not a typical unconfined aerial explosion ignited by a spark or flame. Instead, part of the cloud entered a warehouse and was ignited by a spark. The warehouse explosion became the powerful initiator for the explosion of the unconfined vapor cloud surrounding the warehouse. According to Lewis (1980), this type of explosion may be described as a "quasi-detonation;" the damage is much nearer to that observed with a condensed phase explosion than the damage given by a typical unconfined aerial explosion. Because the WHAZAN model does not model this type of intensified explosion, the consequence modeling may have underestimated the effects.

### 9.3 Vapor Cloud Fire Results

WHAZAN Model Used. Vapor cloud fires were modeled using WHAZAN by running the linked WHAZAN models to obtain the pool evaporation rate. The pool evaporation rate was used as the release rate for the stand-alone buoyant plume dispersion model. The WHAZAN buoyant plume dispersion model was used to estimate the greatest downwind distances at which a flame will move through a flammable vapor cloud. The greatest distance affected by a vapor cloud fire is assumed to be the distance at which the cloud concentration is equal to the lower flammable limit. Any person located within the limited area covered by the flammable part of the vapor cloud would be engulfed in the ensuing fire and would likely die. For a given downwind distance, the total area (as a function of downwind and crosswind distance) potentially affected by a vapor cloud fire is likely to be much smaller than the area that might be affected by a vapor cloud explosion.

Note that the buoyant plume dispersion model uses the release rate (assumed to be the pool evaporation rate), not the fraction flashed. The results shown here do not include the quantity of gas immediately flashed into vapor on release, but only the quantity that evaporates from a pool after the initial flash. For propylene and n-butane, gases assumed to be liquefied under pressure, the fraction flashed is appreciable (33 percent for propylene, 11 percent for n-butane), indicating the calculated distances for these materials may be understated, because the material that flashes could also be involved in the fire.

Results. Exhibit 12 displays the results of dispersion modeling using WHAZAN for vapor clouds of flammable liquids and gases. The data presented include the downwind and crosswind distances at which the concentration in the cloud is equal to 50 percent of the LFL, the LFL, and twice the LFL. The downwind distance is the maximum distance at which the specified concentration is reached; the crosswind distance is the width of the cloud of flammable vapor at that point. The modeled crosswind distances are much smaller than the downwind distances, roughly 6 percent, for the chemicals and conditions analyzed.

The largest modeled downwind distance results (approximately 1,800 meters) were for a release of 180,000 pounds of ethylene; a 1,000 pound release of p-xylene showed the smallest downwind distance (about 20 meters) results. Ethylene also provided the largest downwind distance and p-xylene the smallest at the other hazard criteria levels analyzed for vapor cloud fires.

Exhibit 13 presents WHAZAN vapor cloud fire results as a graph of quantity released versus distance for instantaneous releases, assuming moderate meteorological conditions and modeling to a concentration equal to 50 percent of the LFL. Distances are clearly not linearly related to the quantity released; i.e., increasing the quantity released by a factor of ten increases the distance by a factor of approximately two and one-half for the chemicals modeled.

Effect of Varying Concentration. Exhibit C-7, in Section C.2 of Appendix C, is a graphical presentation of results based on 50 percent of the LFL, the LFL, and twice the LFL for vapor cloud fires for two hydrocarbons. This analysis was done to determine the sensitivity of the model results to changes in the flammable limit level. Using the LFL rather than 50 percent of the LFL for 100,000 pounds of ethylene lowers the affected distance, as would be expected, but by much less than a factor of two. The effect of changing from the LFL to twice the LFL is even smaller. The data presented in Exhibit 12 show there is relatively little difference in distance based on varying the hazard criteria levels for the other chemicals analyzed.



**Exhibit 12**  
**DISTANCES FOR VAPOR CLOUD FIRES FROM EVAPORATING POOLS**  
**FROM INSTANTANEOUS RELEASES, MODERATE METEOROLOGY\*,**  
**DETERMINED USING WHAZAN**

**Distance in Meters to Three Concentrations**

Chemical(Initial Conditions)	Quantity Released (pounds)	Evaporation Rate (lbs/sec)	1/2 LFL		LFL		2 LFL	
			Downwind Distance (meters)	Crosswind Distance (meters)	Downwind Distance (meters)	Crosswind Distance (meters)	Downwind Distance (meters)	Crosswind Distance (meters)
Ethylene (liquefied by refrigeration 175 K, 1.3 Bars)	1,000	60	203	13	138	9	95	6
	2,500	115	294	18	199	13	135	9
	5,000	190	391	24	264	16	179	11
	7,500	254	462	28	311	19	211	13
	10,000	313	522	31	351	21	237	15
	25,000	611	768	45	514	31	346	21
	50,000	1,012	1,030	58	688	40	462	28
	100,000	1,678	1,390	77	925	53	618	36
	180,000	2,580	1,810	97	1,190	67	793	46
Propylene (liquefied under pressure 293 K, 13.3 Bars)	1,000	20	106	7	74	5	60	4
	2,500	42	158	10	107	7	87	6
	5,000	68	207	13	141	9	112	7
	7,500	90	242	15	164	10	131	9
	10,000	110	270	17	184	12	147	9
	25,000	214	394	24	266	17	212	13
	50,000	353	527	31	354	22	281	17
	100,000	587	705	41	473	28	375	23
	180,000	900	905	52	605	36	479	29
Propane (liquefied by refrigeration 232 K, 1.3 Bars)	1,000	24	112	7	77	5	55	4
	2,500	49	162	10	110	7	77	5
	5,000	79	214	13	145	9	99	7
	7,500	108	254	16	172	11	117	8
	10,000	132	285	18	193	12	131	9
	25,000	260	417	25	282	17	191	12
	50,000	430	557	33	375	23	253	16
	100,000	712	747	43	500	30	337	21
	180,000	1,091	959	54	640	38	430	26

\* Wind speed 3.0 meters per second, atmospheric stability class D.

Exhibit 12 (continued)

**DISTANCES FOR VAPOR CLOUD FIRES FROM EVAPORATING POOLS  
FROM INSTANTANEOUS RELEASES, MODERATE METEOROLOGY\*,  
DETERMINED USING WHAZAN**

**Distance in Meters to Three Concentrations**

Chemical(Initial Conditions)	Quantity Released (pounds)	Evaporation Rate (lbs/sec)	1/2 LFL		LFL		2 LFL	
			Downwind Distance (meters)	Crosswind Distance (meters)	Downwind Distance (meters)	Crosswind Distance (meters)	Downwind Distance (meters)	Crosswind Distance (meters)
n-Butane (liquefied under pressure 293 K, 6.3 Bars)	1,000	11	73	5	49	3	35	2
	2,500	24	103	7	73	5	52	3
	5,000	40	135	9	93	6	66	4
	7,500	53	159	10	108	7	76	5
	10,000	64	178	11	120	8	84	6
	25,000	126	259	16	175	11	119	8
	50,000	209	345	21	233	15	158	10
	100,000	346	460	28	309	19	209	13
	180,000	534	588	35	396	24	267	17
Pentane (293 K, 2.74 Bars)	1,000	7	53	4	38	3	27	2
	2,500	15	81	5	57	4	41	3
	5,000	24	101	7	72	5	51	3
	7,500	33	120	8	84	6	59	4
	10,000	40	133	9	92	6	65	4
	25,000	77	193	12	131	9	90	6
	50,000	128	256	16	173	11	118	8
	100,000	212	341	21	230	14	156	10
	180,000	326	435	26	294	18	199	13
Gasoline (293 K, 1.013 Bars)	1,000	7	55	4	39	3	28	2
	2,500	13	78	5	55	4	39	3
	5,000	22	100	7	71	5	50	3
	7,500	29	115	8	81	5	57	4
	10,000	35	132	9	89	6	63	4
	25,000	71	191	12	130	8	89	6
	50,000	117	254	16	172	11	117	8
	100,000	194	338	21	228	14	155	10
	180,000	298	431	26	290	18	196	12

Wind speed 3.0 meters per second, atmospheric stability class D.

Exhibit 12 (continued)

**DISTANCES FOR VAPOR CLOUD FIRES FROM EVAPORATING POOLS  
FROM INSTANTANEOUS RELEASES, MODERATE METEOROLOGY\*,  
DETERMINED USING WHAZAN**

**Distance in Meters to Three Concentrations**

Chemical(Initial Conditions)	Quantity Released (pounds)	Evaporation Rate (lbs/sec)	1/2 LFL		LFL		2 LFL	
			Downwind Distance (meters)	Crosswind Distance (meters)	Downwind Distance (meters)	Crosswind Distance (meters)	Downwind Distance (meters)	Crosswind Distance (meters)
Hexane (293 K, 1.013 Bars)	1,000	4	41	3	29	2	21	1
	2,500	9	58	4	41	3	29	2
	5,000	13	71	5	50	3	36	2
	7,500	18	82	5	58	4	41	3
	10,000	22	91	6	65	4	46	3
	25,000	44	133	9	91	6	65	4
	50,000	73	176	11	119	8	83	6
	100,000	121	233	15	158	10	108	7
	180,000	185	297	18	201	13	136	9
Heptane (293 K, 1.013 Bars)	1,000	2	29	2	21	1	15	1
	2,500	4	41	3	29	2	21	1
	5,000	9	58	4	41	3	29	2
	7,500	11	65	4	46	3	33	2
	10,000	13	71	5	50	3	36	2
	25,000	26	99	7	71	5	50	3
	50,000	42	130	9	89	6	63	4
	100,000	71	173	11	118	8	82	5
	180,000	108	219	14	150	10	101	7
Toluene (293 K, 1.013 Bars)	1,000	2	31	2	22	1	16	1
	2,500	4	43	3	31	2	22	1
	5,000	7	53	4	37	2	27	2
	7,500	9	61	4	43	3	31	2
	10,000	9	64	4	43	3	31	2
	25,000	20	89	6	64	4	46	3
	50,000	33	117	8	83	6	59	4
	100,000	53	154	10	105	7	74	5
	180,000	82	196	12	134	9	92	6

\* Wind speed 3.0 meters per second, atmospheric stability class D.

**Exhibit 12 (continued)**  
**DISTANCES FOR VAPOR CLOUD FIRES FROM EVAPORATING POOLS**  
**FROM INSTANTANEOUS RELEASES, MODERATE METEOROLOGY\*,**  
**DETERMINED USING WHAZAN**

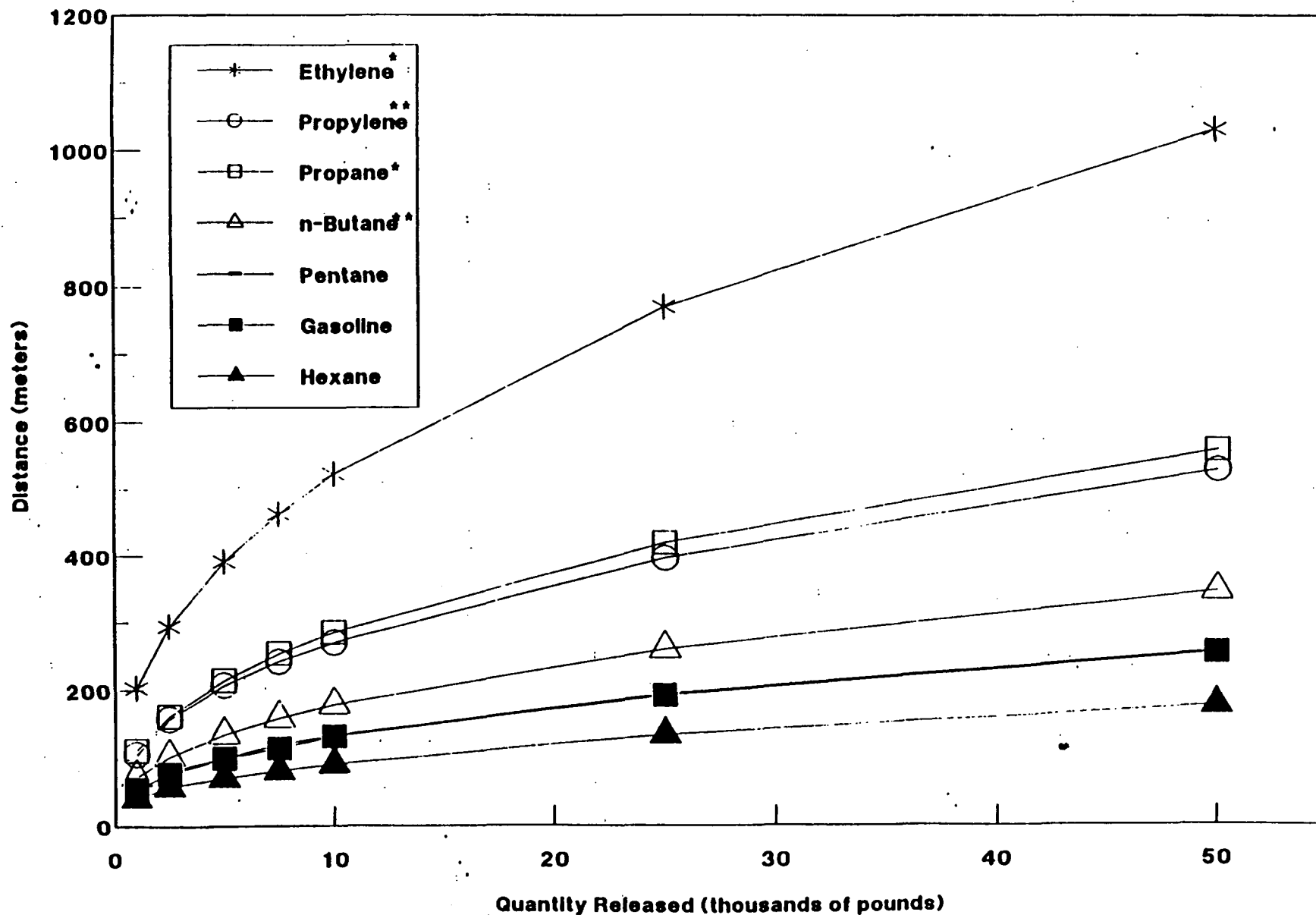
**Distance in Meters to Three Concentrations**

Chemical(Initial Conditions)	Quantity Released (pounds)	Evaporation Rate (lbs/sec)	1/2 LFL		LFL		2 LFL	
			Downwind Distance (meters)	Crosswind Distance (meters)	Downwind Distance (meters)	Crosswind Distance (meters)	Downwind Distance (meters)	Crosswind Distance (meters)
p-Xylene (293 K, 1.013 Bars)	1,000	1	21	1	15	1	11	1
	2,500	2	30	2	21	1	15	1
	5,000	4	42	3	30	2	21	1
	7,500	4	42	3	30	2	21	1
	10,000	7	48	3	36	2	26	2
	25,000	11	67	4	47	3	33	2
	50,000	20	86	6	63	4	44	3
	100,000	31	111	7	78	5	55	4
	180,000	49	141	9	97	7	69	5

Wind speed 3.0 meters per second, atmospheric stability class D.

**Exhibit 13**  
**QUANTITY RELEASED VERSUS DISTANCE**  
**FOR VAPOR CLOUD FIRES, INSTANTANEOUS**  
**RELEASES, MODERATE METEOROLOGY**

**WHAZAN Modelling for 1,000-50,000 Pounds, 50% LFL**



\* Liquefied by refrigeration  
 \*\* Liquefied under pressure

Modeling Using Other Meteorological Conditions. WHAZAN modeling was also carried out for the ten chemicals shown in Exhibit 11 using additional meteorological conditions of wind speed of 1.5 meters per second and F atmospheric stability as inputs, for comparison with the results obtained using the average meteorological conditions. The WHAZAN results for vapor cloud fires appear to be strongly dependent on the meteorological assumptions made, with distances determined using worst case meteorology being much greater than those resulting from modeling using moderate meteorology. Distances for a concentration equal to 50 percent of the LFL under worst case meteorological conditions extend from 1,790 to 6,350 meters for gases, compared to 460 to 1,390 meters under moderate conditions. These results are presented in Exhibit D-1, Appendix D.

Prolonged and Instantaneous Releases. Exhibit D-1, Appendix D, also includes results of WHAZAN modeling for prolonged releases of ten chemicals, where release was assumed to take place from 1.5 inch diameter holes in 12 foot diameter tanks. Distances to the 50 percent of the LFL level for vapor cloud fires are much smaller (18 to 79 meters) than for instantaneous releases, indicating that using instantaneous release conditions is, in general, more conservative than using prolonged release conditions.

Issues. Results of dispersion modeling can vary greatly depending on assumptions used. Meteorological conditions can have a very large effect. In addition, the results presented in Exhibit 12 are based on the assumption that the cloud of flammable vapor ignites when it has reached the maximum distance to the specified concentration; in an actual incident, ignition might occur at any time following the release, or the cloud could disperse without igniting.

#### 9.4 BLEVE Results

WHAZAN Model Used. BLEVE results were obtained using the linked WHAZAN models; the stand-alone BLEVE model was found to give the same results. The WHAZAN default combustion efficiency factor of 0.263 was assumed.

Results. Exhibit 14 presents WHAZAN modeling results for BLEVEs of gases (ethylene, propylene, propane, and n-butane) and for pentane, a volatile liquid assumed to be stored under pressure, for release quantities of 1,000 pounds to 180,000 pounds. Distances for three levels of heat radiation and the duration of the BLEVEs are shown. These data are all important components in analyzing the consequences of BLEVEs, which are a function of exposure to heat radiation levels for the duration of the resulting fireball. As noted in Section 6.1.3, pentane and lighter hydrocarbons have characteristics (i.e., 10 percent of the chemical vaporizes when it is released to the atmosphere from a vessel) that give them a high potential to be involved in BLEVEs (Nazario 1988). While heavier hydrocarbons may be subject to BLEVEs under some conditions, the likelihood of occurrence of a BLEVE is much smaller for such chemicals; therefore, WHAZAN BLEVE results for hydrocarbons heavier than pentane are not included in Exhibit 14.

The most volatile of the chemicals analyzed, ethylene, shows the greatest distances, and the least volatile, pentane, the smallest; however, distances do not vary greatly from chemical to chemical. For release quantities of less than 10,000 pounds, at a heat radiation level of 12.5 kW/m<sup>2</sup>, distances for ethylene vary from 82 meters for 1,000 pounds to 179 meters for 10,000 pounds. For pentane, the range is 56 meters for 1,000 pounds to 120 meters for 10,000 pounds.

**Exhibit 14**  
**DISTANCES FOR BLEVES**  
**FOR INSTANTANEOUS RELEASES OF 1,000 TO 180,000 POUNDS**  
**DETERMINED USING WHAZAN**

Distance in Meters to Three Heat Radiation Levels

Chemical (Initial Conditions)	Quantity Released (pounds)	Distance in Meters to the Following Heat Radiation Levels			BLEVE *Duration (seconds)
		4.0 kW/m <sup>2</sup>	12.5 kW/m <sup>2</sup>	37.5 kW/m <sup>2</sup>	
Ethylene (liquefied by refrigeration 175 K, 1.3 Bars)	1,000	146	82	47	8
	2,500	198	112	65	11
	5,000	250	141	82	14
	7,500	287	162	94	16
	10,000	316	179	103	17
	25,000	430	243	140	23
	50,000	543	307	177	29
	100,000	685	388	224	36
	180,000	835	472	273	44
Propylene (liquefied under pressure 293 K, 13.3 Bars)	1,000	108	61	35	8
	2,500	147	83	48	11
	5,000	185	105	60	14
	7,500	212	120	69	16
	10,000	234	132	76	17
	25,000	318	180	104	23
	50,000	402	227	131	29
	100,000	508	287	166	36
	180,000	618	350	202	44
Propane (liquefied by refrigeration 232 K, 1.3 Bars)	1,000	104	59	34	8
	2,500	142	80	46	11
	5,000	179	102	59	14
	7,500	206	116	67	16
	10,000	227	128	74	17
	25,000	308	174	101	23
	50,000	389	220	127	29
	100,000	492	278	161	36
	180,000	599	339	196	44

Exhibit 14 (continued)  
**DISTANCES FOR BLEVES**  
**FOR INSTANTANEOUS RELEASES OF 1,000 TO 180,000 POUNDS**  
**DETERMINED USING WHAZAN**

Chemical (Initial Conditions)	Quantity Released (pounds)	Distance in Meters to the Following Heat Radiation Levels			BLEVE Duration (seconds)
		4.0 kW/m <sup>2</sup>	12.5 kW/m <sup>2</sup>	37.5 kW/m <sup>2</sup>	
n-Butane (liquefied under pressure 293 K, 6.3 Bars)	1,000	101	57	33	8
	2,500	137	78	45	11
	5,000	173	98	57	14
	7,500	199	112	65	16
	10,000	219	124	72	17
	25,000	298	169	97	23
	50,000	376	213	123	29
	100,000	475	269	155	36
	180,000	579	328	189	44
Pentane (293 K, 2.74 Bars)	1,000	101	57	33	8
	2,500	137	78	45	11
	5,000	173	98	57	14
	7,500	199	112	65	16
	10,000	219	124	72	17
	25,000	298	169	97	23
	50,000	376	213	123	29
	100,000	475	269	155	36
	180,000	579	328	189	44



The duration of a BLEVE as estimated by WHAZAN appears to depend only on the quantity released; it does not vary by chemical. For release quantities of 10,000 pounds or less, WHAZAN shows the BLEVE duration to range from 8 seconds for 1,000 pounds to 17 seconds for 10,000 pounds. As noted earlier, the WHAZAN manual (WHAZAN 1988) suggests that at a heat radiation level of  $12.5 \text{ kW/m}^2$ , there would be a 1 percent probability of fatality for a 30 second exposure. Therefore, for BLEVEs lasting less than 30 seconds, as is the case for BLEVEs involving quantities less than 10,000 pounds, a higher heat radiation level might be of greater interest (e.g.,  $37.5 \text{ kW/m}^2$  rather than  $12.5 \text{ kW/m}^2$ ), as exposure could not last longer than 20 seconds. For a heat radiation level of  $37.5 \text{ kW/m}^2$ , distances for ethylene are 39 meters for a 1,000 pound release and 103 meters for a 10,000 pound release.

Exhibit 15 shows WHAZAN results, presented graphically, for BLEVEs of 1,000 to 50,000 pounds of hydrocarbons. The graph of released quantity versus distance indicates that distance is proportional to the cube root of quantity, as was the case for vapor cloud explosions.

Effect of Varying Heat Radiation Levels. Exhibit C-10, in Section C.3.2 of Appendix C, presents BLEVE results, in graphical form, from WHAZAN modeling of two hydrocarbons for three heat radiation levels, to test the model results for sensitivity to varying hazard criteria levels. For ethylene and propylene, using  $37.5 \text{ kW/m}^2$  rather than  $12.5 \text{ kW/m}^2$  appears to have a relatively small effect on results; using  $4 \text{ kW/m}^2$  rather than  $12.5 \text{ kW/m}^2$  appears to have a greater effect.

Modeling Using Other Meteorological Conditions. WHAZAN modeling was also carried out for BLEVEs using worst case meteorological conditions. Varying the meteorological conditions appeared to have no effect; results obtained were identical to the results obtained using moderate meteorological conditions, indicating that meteorological conditions would be expected to have little impact on the consequences of BLEVEs. Results are presented in Exhibit D-1, Appendix D.

Prolonged and Instantaneous Releases. WHAZAN modeling assuming a prolonged release for a BLEVE gave results identical to those assuming an instantaneous release, as shown in Exhibit D-1, Appendix D. As BLEVEs result from sudden vessel failure, they would always be essentially instantaneous; therefore, it is not clear that any distinction can be made between instantaneous versus prolonged release input in modeling BLEVEs.

Issues. As discussed above, the duration of the fireball from a BLEVE, as well as the heat intensity, is an important consideration for estimating potential consequences of a BLEVE.

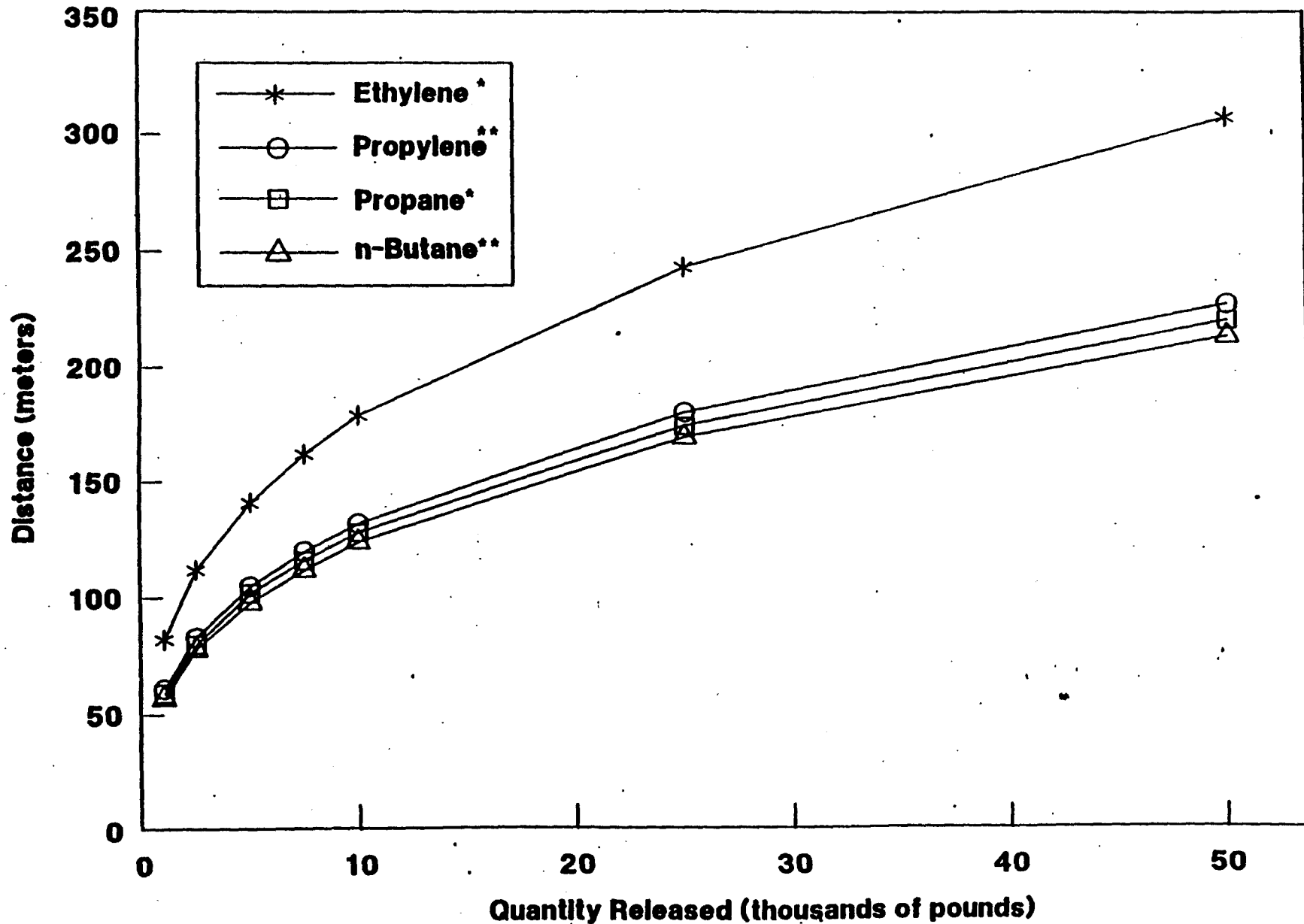
In addition to the heat radiation effects, BLEVEs can also result in projectiles. Section 6.6 discusses the characteristics and hazards of projectiles from BLEVEs. The distances affected by projectiles may be larger than the distances affected by heat radiation; for example, calculations presented by AIChE (1987) (see Exhibit 7) show a 150 pound vessel fragment thrown more than 1,000 meters from a 3,000 gallon reactor. This distance is greater than distances calculated to any heat radiation level by WHAZAN modeling. The distances traveled and the potential effects of projectiles, however, are more localized, explosion/site specific, and unpredictable.

## 9.5 Pool Fire Results

WHAZAN Model Used. The WHAZAN linked models were used to obtain pool fire results. For substances that are gases under ambient conditions, the linked models calculate the fraction flashed and treat the remaining liquid as a circular pool that spreads to maximum size. For liquids, the entire quantity released is assumed to be in the pool. The WHAZAN default value for combustion efficiency of 0.35 was assumed.

Exhibit 15  
QUANTITY RELEASED VERSUS DISTANCE  
FOR BLEVES, INSTANTANEOUS RELEASES

WHAZAN Modelling for 1,000-50,000 Pounds, 12.5 kW/m<sup>2</sup>



\* Liquefied by refrigeration  
\*\* Liquefied under pressure

Results. Exhibit 16 presents WHAZAN modeling results for pool fires resulting from releases of 1,000 to 180,000 pounds of ten hydrocarbons. Distances are given for three levels of heat radiation. The initial quantity in the pool and the duration of the fire are also provided.

For all the chemicals shown in Exhibit 16, distances for releases smaller than 10,000 pounds are less than 100 meters. The distance results for pool fires do not vary greatly by chemical, possibly because all of the chemicals shown here are hydrocarbons, and all have similar heats of combustion. (WHAZAN produced somewhat smaller distances for a given quantity of several organic chemicals with differing heats of combustion; see Exhibit D-1, Appendix D.) Ethylene and propane, the two gases assumed liquefied by refrigeration, show greater distances than propylene and n-butane, gases assumed to be liquefied under pressure. Larger quantities of the pressurized gases flash into vapor on release than for the refrigerated gases; therefore, the quantity in the pool would be larger for the refrigerated gases, and the greater distances would be expected.

The pool fire duration data range from about 20 seconds for 1,000 pounds of propylene to approximately 2 minutes for 180,000 pounds of p-xylene. After that time the material in the pool is consumed, extinguishing the pool fire. The data for a specific quantity and hazard criteria level are fairly consistent from chemical to chemical.

The WHAZAN pool fire results are presented graphically in Exhibit 17 for releases of 1,000 to 50,000 pounds. The graph of quantity released versus distance indicates that distance is proportional to the cube root of the quantity released, as was the case for vapor cloud explosions and BLEVEs.

Effect of Varying Heat Radiation Levels. Exhibit C-11, in Section C.3.2 of Appendix C, presents WHAZAN modeling results, in graphical form, for ethylene and propylene, showing the effect of using different heat radiation levels. As was the case for BLEVEs, using a different heat radiation level appears to have a greater effect on distance at lower levels than at higher levels. The graph indicates that basing results on  $10 \text{ kW/m}^2$ , as in ARCHIE modeling (see Exhibit D-1, Appendix D), rather than  $12.5 \text{ kW/m}^2$ , probably does not have a great effect on the results.

Modeling Using Other Meteorological Conditions. WHAZAN modeling of pool fires for ten chemicals using worst case meteorology gave results identical to those obtained using moderate meteorology, indicating that meteorological conditions probably do not have much effect on pool fire consequences. These results are presented in Exhibit D-1, Appendix D.

Prolonged and Instantaneous Releases. WHAZAN pool fire results for prolonged releases (assuming release from a hole with a diameter of 1.5 inches) of 100,000 pounds of ten chemicals are presented in Exhibit D-1, Appendix D; results for instantaneous releases are also included for comparison. Distances for prolonged releases are much smaller (9 to 23 meters compared to 152 to 182 meters) than for instantaneous releases, again indicating that the input of instantaneous release type is more conservative than assuming a prolonged release.

**Exhibit 16**  
**DISTANCES FOR POOL FIRES**  
**FOR INSTANTANEOUS RELEASES OF 1,000 TO 180,000 POUNDS**  
**DETERMINED USING WHAZAN**

**Distance in Meters to Three Heat Radiation Levels**

Chemical (Initial Conditions)	Quantity Released (pounds)	Quantity In Pool (pounds)	Pool Fire Radius (meters)	Distance in Meters to the Following Heat Radiation Levels :			Pool Fire Duration (seconds)
				1.6 kW/m <sup>2</sup>	4.0 kW/m <sup>2</sup>	12.5 kW/m <sup>2</sup>	
Ethylene (liquefied by refrigeration 175 K, 1.3 Bars)	1,000	977	11	112	72	40	26
	2,500	2,448	15	151	96	54	32
	5,000	5,000	19	190	120	68	38
	7,500	7,321	23	217	137	77	42
	10,000	9,768	25	238	150	85	45
	25,000	24,476	36	321	203	115	57
	50,000	46,526	46	403	255	144	68
	100,000	97,682	60	506	320	181	81
	180,000	175,739	74	614	388	220	94
Propylene (liquefied under pressure 293 K, 13.3 Bars)	1,000	650	9	100	63	36	22
	2,500	1,678	13	136	86	49	28
	5,000	3,352	17	170	108	61	33
	7,500	5,027	20	194	123	69	36
	10,000	6,483	21	211	133	75	39
	25,000	16,229	30	284	180	102	49
	50,000	32,414	39	356	225	128	58
	100,000	64,827	51	447	283	160	69
	180,000	116,865	64	542	343	194	80
Propane (liquefied by refrigeration 232 K, 1.3 Bars)	1,000	986	10	114	72	41	25
	2,500	2,470	15	153	97	55	31
	5,000	4,917	19	192	121	69	37
	7,500	7,387	22	219	139	78	41
	10,000	9,856	25	241	152	86	44
	25,000	24,696	35	324	205	116	55
	50,000	49,172	45	407	257	146	65
	100,000	98,564	58	511	323	183	78
	180,000	177,282	73	620	392	222	90
n-Butane (liquefied under pressure 293 K, 6.3 Bars)	1,000	858	10	110	70	39	23
	2,500	2,227	14	150	95	54	29
	5,000	5,005	18	188	119	67	35
	7,500	6,659	21	214	135	77	38
	10,000	8,577	23	232	147	83	41
	25,000	21,433	32	313	198	112	51
	50,000	42,777	42	393	249	141	61
	100,000	85,775	54	493	312	176	73
	180,000	154,350	67	598	378	214	84

**Exhibit 16 (continued)**  
**DISTANCES FOR POOL FIRES**  
**FOR INSTANTANEOUS RELEASES OF 1,000 TO 180,000 POUNDS**  
**DETERMINED USING WHAZAN**

**Distance in Meters to Three Heat Radiation Levels**

Chemical (Initial Conditions)	Quantity Released (pounds)	Quantity In Pool (pounds)	Pool Fire Radius (meters)	Distance in Meters to the Following Heat Radiation Levels			Pool Fire Duration (seconds)
				1.6 kW/m <sup>2</sup>	4.0 kW/m <sup>2</sup>	12.5 kW/m <sup>2</sup> *	
Pentane (293 K, 2.74 Bars)	1,000	1,000	10	114	72	41	25
	2,500	2,500	14	153	97	55	31
	5,000	5,000	19	192	121	69	37
	7,500	7,500	22	219	138	78	41
	10,000	10,000	24	240	152	86	44
	25,000	25,000	34	324	205	116	55
	50,000	50,000	45	406	257	145	66
	100,000	100,000	58	510	322	182	78
	180,000	180,000	72	618	391	221	91
Gasoline (293 K, 1.013 Bars)	1,000	1,000	10	109	69	39	26
	2,500	2,500	14	146	93	52	33
	5,000	5,000	18	184	116	66	39
	7,500	7,500	22	209	132	75	43
	10,000	10,000	24	230	145	82	46
	25,000	25,000	34	310	196	111	58
	50,000	50,000	44	389	246	139	69
	100,000	100,000	57	488	309	175	82
	180,000	180,000	71	592	375	212	95
Hexane (293 K, 1.013 Bars)	1,000	1,000	11	108	69	39	27
	2,500	2,500	15	146	92	52	34
	5,000	5,000	19	183	116	65	40
	7,500	7,500	22	209	132	75	44
	10,000	10,000	25	229	145	82	48
	25,000	25,000	35	309	196	111	60
	50,000	50,000	46	388	246	139	71
	100,000	100,000	59	488	308	174	85
	180,000	180,000	74	592	374	212	98
Heptane (293 K, 1.013 Bars)	1,000	1,000	11	104	66	37	29
	2,500	2,500	15	140	88	50	36
	5,000	5,000	20	175	111	63	43
	7,500	7,500	23	200	127	72	48
	10,000	10,000	26	220	139	79	52
	25,000	25,000	36	297	188	106	65
	50,000	50,000	47	373	236	134	77
	100,000	100,000	61	469	297	168	92
	180,000	180,000	76	569	360	204	106

Exhibit 16 (continued)

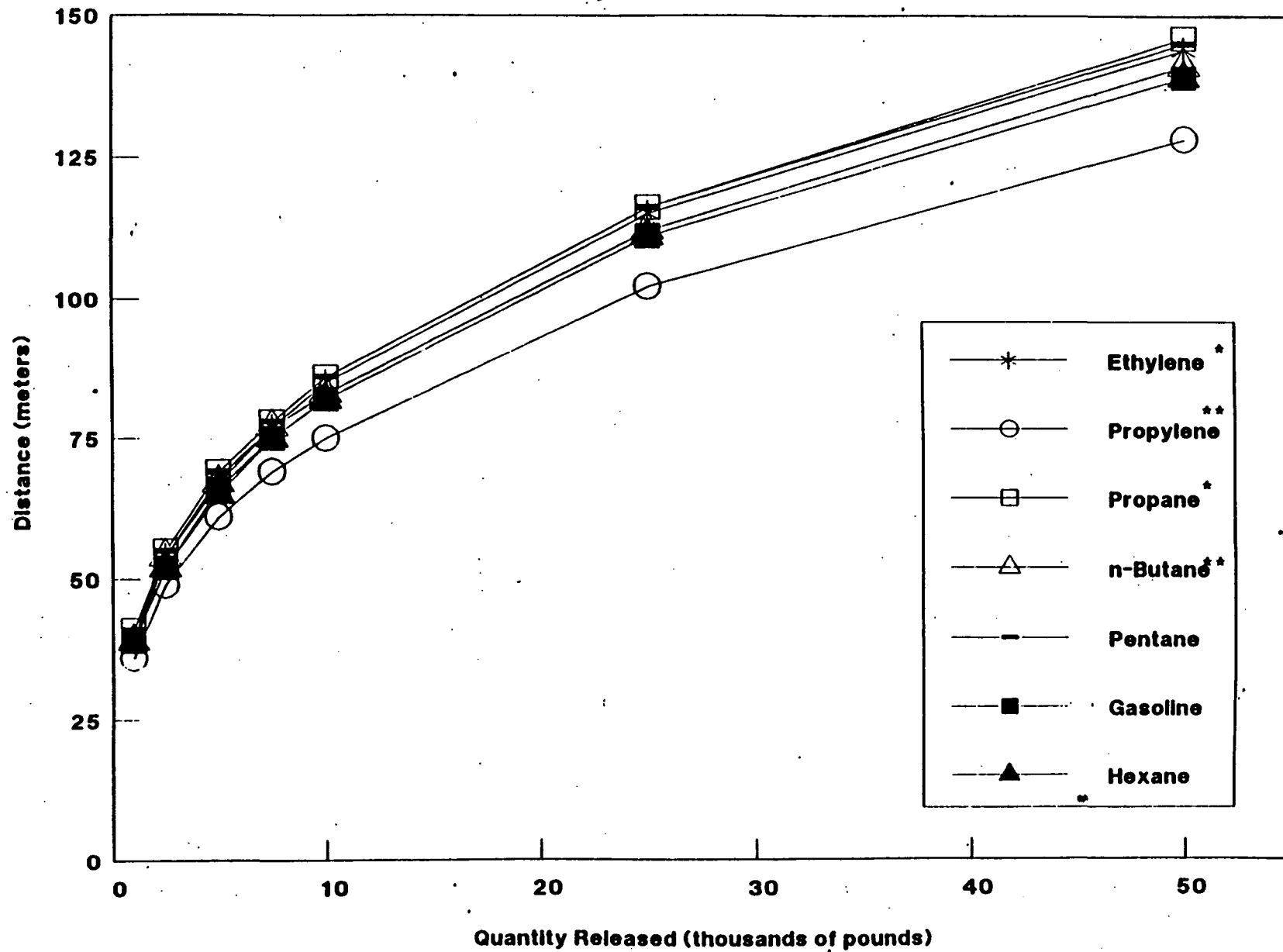
**DISTANCES FOR POOL FIRES  
FOR INSTANTANEOUS RELEASES OF 1,000 TO 180,000 POUNDS  
DETERMINED USING WHAZAN**

**Distance in Meters to Three Heat Radiation Levels**

Chemical (Initial Conditions)	Quantity Released (pounds)	Quantity In Pool (pounds)	Pool Fire Radius (meters)	Distance in Meters to the Following Heat Radiation Levels			Pool Fire Duration (seconds)
				1.6 kW/m <sup>2</sup>	4.0 kW/m <sup>2</sup>	12.5 kW/m <sup>2</sup>	
Toluene (293 K, 1.013 Bars)	1,000	1,000	11	95	60	34	32
	2,500	2,500	15	128	81	46	40
	5,000	5,000	20	160	101	57	48
	7,500	7,500	23	183	116	65	53
	10,000	10,000	26	201	127	72	57
	25,000	25,000	36	272	172	97	71
	50,000	50,000	47	338	214	121	87
	100,000	100,000	60	429	271	153	100
	180,000	180,000	75	520	329	186	117
p-Xylene (293 K, 1.013 Bars)	1,000	1,000	11	94	59	34	33
	2,500	2,500	15	127	80	45	41
	5,000	5,000	20	159	101	57	49
	7,500	7,500	23	181	115	65	54
	10,000	10,000	26	199	126	71	58
	25,000	25,000	37	269	170	96	73
	50,000	50,000	47	338	214	121	87
	100,000	100,000	61	425	269	152	103
	180,000	180,000	76	517	327	185	119

Exhibit 17  
QUANTITY RELEASED VERSUS DISTANCE  
FOR POOL FIRES, INSTANTANEOUS RELEASES

WHAZAN Modelling for 1,000-50,000 Pounds, 12.5 kW/m<sup>2</sup>



\* Liquified by refrigeration

\*\* Liquified under pressure

## 9.6 Jet Fire Results

Exhibit 18 presents WHAZAN results for jet fires, which are defined by the model as prolonged releases. Results were obtained only for two gases (propylene and n-butane) assumed to be stored under pressure at ambient temperature. Results for releases of 10,000 pounds and three heat radiation levels are shown along with the duration of the jet fire. Distances for 10,000 pound releases of n-butane were less than 25 meters for all three heat radiation levels modeled. For propylene, the distances ranged from 35 meters at  $37.5 \text{ kW/m}^2$  to 51 meters at  $4.0 \text{ kW/m}^2$ . The duration of the release (and presumably of the jet fire) would be approximately one hour for the n-butane jet fire and about 15 minutes for the propylene jet fire. For both of these gases, the other types of accidents modeled gave much greater distances than jet fires. As detailed in Exhibit D-1, Appendix D, jet fires for 100,000 pound releases of n-butane and propylene produce distance results almost identical to the results for 10,000 pound releases. However, the duration of the jet fires for the 100,000 pound releases was much greater. Note that for an instantaneous release of these gases, the possible result would be a vapor cloud explosion or fire, not a jet fire.

## 10.0 Findings

WHAZAN model results seemed to closely correlate with overpressure data from actual vapor cloud explosions. This helps to support the use of the WHAZAN model to predict consequences of vapor cloud explosions. Based on the results of modeling flammable hazards using the WHAZAN model and analysis of the literature, a clear distinction can be made between the results for flammable substances that boil at higher temperatures than pentane and flammable substances that boil at lower temperatures than pentane. This would suggest a distinction exists at roughly  $310^\circ\text{K}$  -  $315^\circ\text{K}$  ( $37^\circ\text{C}$  -  $42^\circ\text{C}$ ). Analysis of other classification schemes and regulations (see Section 3) shows that flammable gases and volatile flammable liquids appear to be the flammable materials considered of greatest concern by agencies and organizations such as DOT, NFPA, and EEC. The temperature at which clear distinctions in consequences can be made corresponds to the temperature at which DOT and NFPA have made distinctions in categories of flammable materials (boiling point below  $38^\circ\text{C}$  and flash point below  $23^\circ\text{C}$  for NFPA flammability rating 4; boiling point below  $35^\circ\text{C}$  and flash point below  $23^\circ\text{C}$  for DOT Packing Group I). This temperature also corresponds to very high ambient temperatures ( $38^\circ\text{C}$  is roughly  $100^\circ\text{F}$ ); it is possible for substances with boiling points less than  $37^\circ\text{C}$  -  $42^\circ\text{C}$  to be gases under ambient conditions. Therefore, flammable gases and very volatile flammable liquids (including substances that boil at temperatures less than about  $42^\circ\text{C}$ ) appear to be the most likely candidates for further consideration.

Exhibit 19 identifies 69 flammable gases (boiling point at or below  $20^\circ\text{C}$ ). This list includes most flammable gases currently in commerce. Eight of these substances are regulated as extremely hazardous substances (EHSs) on the basis of toxicity and are indicated in the exhibit by an asterisk. The substances in this exhibit are gases that have NFPA flammability ratings of 4 (NFPA 1984) or are listed by DOT as flammable gases in current DOT regulations (U.S. DOT 1984) or in DOT's proposed rule (U.S. DOT 1987). (Note that there are discrepancies in the ratings of a few chemicals, e.g., vinyl bromide is listed as a flammable gas by DOT but considered non-flammable by the NFPA.) Liquids that boil close to ambient temperature may vaporize readily and also may form vapor clouds. If the flash points of such liquids are at or below ambient temperature, the vapor may ignite under ambient conditions and vapor cloud fires or explosions may occur. Exhibit 20 shows 28 liquids that boil below  $38^\circ\text{C}$  and have flash points lower than  $23^\circ\text{C}$  (i.e., their flash points are at or below normal ambient temperature). Three of them (indicated by an asterisk in the exhibit) are listed as EHSs because of toxicity. The substances in this exhibit have NFPA flammability ratings of 4 (NFPA 1984) or appear to meet the criteria for this rating on the basis of flash point and boiling point.



**Exhibit 18**  
**DISTANCES FOR JET FIRES**  
**FOR PROLONGED RELEASES OF 10,000 POUNDS**  
**DETERMINED USING WHAZAN**

Chemical (Initial Conditions)	Quantity Released (pounds)	Distance in Meters to the Following Heat Radiation Levels			Jet Fire Duration (seconds)
		4.0 kW/m <sup>2</sup>	12.5 kW/m <sup>2</sup>	37.5 kW/m <sup>2</sup>	
Propylene (liquefied under pressure 293 K, 13.3 Bars)	10,000	51	40	35	15
n-Butane (liquefied under pressure 293 K, 6.3 Bars)	10,000	25	19	17	60

Exhibit 19  
FLAMMABLE GASES

<u>CAS #</u>	<u>Chemical</u>	<u>Boiling Point (°C)</u>
74-86-2	ACETYLENE	-83
7784-42-1	ARSINE*	-63
598-73-2	BROMOTRIFLUORETHYLENE	
75-63-8	BROMOTRIFLUOROMETHANE	-59
106-99-0	1,3-BUTADIENE	-4.4
75-28-5	ISOBUTANE	-12
106-97-8	BUTANE	-0.5
590-18-1	2-BUTENE-CIS	3.7
624-64-6	2-BUTENE-TRANS	0.9
106-98-9	ALPHA-BUTYLENE	-6.5
107-01-7	BETA-BUTYLENE	1.0
25167-67-3	BUTYLENE	-6.3
630-08-0	CARBON MONOXIDE	-192
463-58-1	CARBON OXYSULFIDE	-50
7791-21-1	CHLORINE MONOXIDE	4
460-19-5	CYANOGEN	-21
506-77-4	CYANOGEN CHLORIDE	13
287-23-0	CYCLOBUTANE	13
75-19-4	CYCLOPROPANE	-33
7782-39-0	DEUTERIUM	-250
19287-45-7	DIBORANE*	-93
4109-96-0	DICHLOROSILANE	8.3
75-68-3	DIFLUORO-1-CHLOROETHANE	-9
75-37-6	DIFLUOROETHANE	-25
124-40-3	DIMETHYLAMINE	7
463-82-1	2,2-DIMETHYLPROPANE	9.5
74-84-0	ETHANE	-89
107-00-6	ETHYL ACETYLENE	
75-04-7	ETHYLAMINE	17
75-00-3	ETHYL CHLORIDE	12
74-85-1	ETHYLENE	-104
75-21-8	ETHYLENE OXIDE*	11
353-36-6	ETHYL FLUORIDE	-38
540-67-0	ETHYL METHYL ETHER	11
109-95-5	ETHYL NITRITE	17
50-00-0	FORMALDEHYDE*	-20
7782-65-2	GERMANE	-88
1333-74-0	HYDROGEN	-253
7783-07-5	HYDROGEN SELENIDE*	-41
7783-06-4	HYDROGEN SULFIDE*	-60

\*EHS

Exhibit 19  
FLAMMABLE GASES (continued)

<u>CAS #</u>	<u>Chemical</u>	<u>Boiling Point (°C)</u>
64741-48-6	LIQUEFIED NATURAL GAS	-159
68476-85-7	LIQUEFIED PETROLEUM GAS	-40
74-82-8	METHANE	-162
74-89-5	METHYLAMINE	-6.3
563-45-1	3-METHYL-1-BUTENE	20
74-87-3	METHYL CHLORIDE	-24
115-10-6	METHYL ETHER	-24
593-53-3	METHYL FLUORIDE	
74-93-1	METHYL MERCAPTAN*	6
115-11-7	2-METHYLPROPENE	-7
8006-14-2	NATURAL GAS	
68476-26-6	OIL GAS	
504-60-9	1,3-PENTADIENE	-43
7803-51-2	PHOSPHINE*	-88
463-49-0	PROPADIENE	-35
74-98-6	PROPANE	-42
115-07-1	PROPYLENE	-48
74-99-7	PROPYNE	-23
7803-62-5	SILANE	-111
116-14-3	TETRAFLUOROETHYLENE	-76
79-38-9	TRIFLUOROCHLOROETHYLENE	-28
420-46-2	1,1,1-TRIFLUOROETHANE	-48
75-50-3	TRIMETHYLAMINE	3
689-97-4	VINYL ACETYLENE	5
593-60-2	VINYL BROMIDE	16
75-01-4	VINYL CHLORIDE	-13
75-02-5	VINYL FLUORIDE	-72
75-38-7	VINYLDENE FLUORIDE	-83
107-25-5	VINYL METHYL ETHER	12

\*EHS

Sources: NFPA 1984, U.S. DOT 1984, U.S. DOT 1987.

**Exhibit 20**  
**FLAMMABLE, VOLATILE LIQUIDS**

CAS #	Chemical	Boiling Point (°C)	Flash Point (°C)
75-07-0	ACETALDEHYDE	20	-36
627-20-3	AMYLENE, beta-,cis	37	<-20
646-04-8	AMYLENE, beta-,trans	36	<-20
75-91-2	TERT-BUTYL HYDROPEROXIDE	35	<27
503-17-3	2-BUTYNE	27	<-20
557-98-2	2-CHLOROPROPYLENE	23	<-20
590-21-6	1-CHLOROPROPYLENE	33	<-6
75-18-3	DIMETHYL SULFIDE	37	-38
60-29-7	ETHYL ETHER	35	-45
75-08-1	ETHYL MERCAPTAN	34	-18
110-00-9	FURAN*	32	
74-90-8	HYDROGEN CYANIDE*	26	-18
78-79-5	ISOPRENE	34	-54
	ISOPROPENYL ACETYLENE	33	<-7
563-46-2	2-METHYL-1-BUTENE	31	<-7
563-45-1	3-METHYL-1-BUTENE	37	<-7
107-31-3	METHYL FORMATE	32	-32
78-78-4	ISOPENTANE	28	-57
109-66-0	PENTANE	36	-49
109-67-1	1-PENTENE	30	-18
8030-30-6	PETROLEUM NAPHTHA	35	-18
75-31-0	ISOPROPYLAMINE	32	-26
75-29-6	ISOPROPYL CHLORIDE	36	-32
75-56-9	PROPYLENE OXIDE*	34	-37
75-76-3	TETRAMETHYLSILANE	26	
10025-78-2	TRICHLOROSILANE	32	-14
109-92-2	VINYL ETHYL ETHER	36	-46
75-35-4	VINYLDENE CHLORIDE	32	-28

\*EHS

Sources: NFPA 1984, U.S. DOT 1984, U.S. DOT 1987.

Chemicals with higher boiling points (38°C and above) with flash points at or below ambient temperature will not vaporize readily under ambient conditions, but may ignite and burn. For these chemicals, pool fires are a more likely event than vapor cloud fires and explosions. Modeling indicates that pool fires are less hazardous than vapor cloud fires and explosions, based on the distance results. Over 350 liquids with boiling points of 38°C or higher and flash points below 23°C have been identified, including many common, high-volume substances such as gasoline, benzene, toluene, and the xylenes.

For vapor cloud explosions, BLEVEs, and pool fires, the distance for a given hazard criterion level is proportional to the cube root of the quantity released (i.e., doubling the quantity of chemical used in the analysis does not double the distance, but increases it by a factor of about 1.26, the cube root of 2). For vapor cloud fires, the distance is not directly proportional to quantity; the exact relationship is not known, but the quantity versus distance curve (see Exhibit 13) is similar in shape to the curves showing the cube root relationship (see Exhibits 10, 15, and 17).

For a given quantity of a flammable chemical, distances for all types of accidents depend on the hazard criterion level chosen for use in the analysis; i.e., the overpressure level (for vapor cloud explosions), concentration (for vapor cloud fires), or heat radiation level (for BLEVEs, pool fires, and jet fires). The greatest distances calculated using the WHAZAN model resulted from vapor cloud explosions and vapor cloud fires of gases and very volatile liquids. Vapor cloud explosions have been described as unlikely for clouds containing less than 10,000 pounds of flammable gas (API 1990). As noted earlier, the effects of vapor cloud fires are likely to be limited to a much smaller cross-sectional area than the effects of vapor cloud explosions, since persons would have to be in the path of the engulfing fire for fatalities to occur. The vapor cloud explosion results vary depending on the overpressure considered; at overpressures of 3.0 psi and higher, modeling showed greater distances for BLEVEs than for vapor cloud explosions. Pool fires appear to produce more localized consequences than vapor cloud explosions, vapor cloud fires, and BLEVEs.

The consequence analysis results do not take into account the likelihood that a particular type of consequence, such as a vapor cloud explosion, will result from a particular accident. The specific circumstances surrounding an accident (e.g., amount of material involved; release type, such as storage, processing, transfer, transport) and the specific conditions (e.g., time of day, local meteorology and climate, proximity and type of population) at the time of an accident may have significant effects on the severity and range of consequences. Modeling cannot take all circumstances and conditions into account.

The modeling also indicates that meteorological conditions can have a major effect on the consequences of vapor cloud fires, based on the dispersion of the flammable cloud, which impacts both distance travelled and concentration. Storage temperatures of liquefied gases may have a significant effect on consequence results for gas releases; at extremely cold storage temperatures, much less of the gas will flash on release. Based on the results for prolonged releases under the conditions modeled, it appears that instantaneous releases have consequences at greater distances than prolonged releases.

The greatest distance overall calculated using the WHAZAN model for an instantaneous release of 10,000 pounds was for a vapor cloud explosion of propylene liquefied under pressure. The distance for an overpressure of 0.3 psi was 800 meters; however, this overpressure is probably too low to cause serious injury. For an overpressure of 1.0 psi, modeling produced a distance of 300 meters for a 10,000 pound release of propylene. Note, however, that a 10,000 pound release under the conditions modeled would produce a cloud containing approximately 3,300 pounds of propylene, a quantity that would have a low probability of exploding (Prugh 1987). Vapor cloud fire results for a 10,000 pound release of ethylene, based on dispersion to a concentration equal to 50 percent of the LFL, indicated a downwind distance of 550 meters, which is greater than the vapor cloud explosion distance of 300 meters for 1.0 psi; however, the area within which the vapor cloud would be flammable (and hence fatal to anyone in the fire zone) is

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## APPENDIX A

### ADDITIONAL INFORMATION ON CLASSIFICATION SYSTEMS FOR FLAMMABLE CHEMICALS

#### A.1 Definitions Related to Classification of Flammable Substances

A flammable material is "any solid, liquid, vapor or gas that will ignite easily and burn rapidly. Flammable gases are ignited very easily; the flame and heat propagation rate is so great as to resemble an explosion, especially if the gas is confined. Flammable gases are extremely dangerous fire hazards and require precisely regulated storage conditions" (Sax and Lewis 1987).

The flash point of a chemical is "the temperature at which a liquid or volatile solid gives off a vapor sufficient to form an ignitable mixture with the air near the surface of the liquid or within the test vessel" (NFPA as cited by Sax and Lewis 1987). There are many different methods to measure a chemical's flash point. Examples are the Cleveland Open Cup (COC) and Pensky-Martens methods. Most flash point tests pass a flame just above the surface of the material being tested. The material is heated slowly and the flash point is defined as the temperature at which the vapor generated above the material ignites. Note that because ignition is the test end point, flash point tests can be used as a criterion for determining whether a material is flammable or not. Flash point is also related to a chemical's volatility. Unfortunately, most flash point tests are relatively inaccurate, particularly when applied to viscous liquids (their precision is generally  $\pm 3^\circ\text{F}$  (ASTM 1969)).

The boiling point of a chemical is "the temperature of a liquid at which its vapor pressure is equal to or very slightly greater than the atmospheric pressure of the environment" (Sax and Lewis 1987). Boiling point is an indicator of a chemical's volatility. Boiling point tests are relatively accurate and simple to run.

#### A.2 DOT Classifications

Current DOT classifications for flammable materials are as follows (49 CFR 172):

**Flammable Liquid:** Any liquid having a flash point below  $100^\circ\text{F}$  ( $37.8^\circ\text{C}$ ).

**Combustible Liquid:** Liquid with flash point of  $100^\circ\text{F}$  ( $37.8^\circ\text{C}$ ) or greater, and less than  $200^\circ\text{F}$  ( $93^\circ\text{C}$ ).

**Flammable Solid:** Any solid material, other than an explosive, which under normal transportation conditions is liable to cause fires through friction or retained heat, or which can be ignited readily and burns so vigorously and persistently as to create a serious transportation hazard.

**Flammable Gas:** Compressed gas is defined as a material having pressure greater than 40 psia at  $70^\circ\text{F}$ , or pressure greater than 104 psia at  $130^\circ\text{F}$ , or a flammable liquid, vapor pressure greater than 40 psia at  $100^\circ\text{F}$ ; a compressed gas is classed as flammable if mixture of 13% or less by volume with air forms flammable mixture or flammable range is wider than 12%, or it is shown to be explosive or flammable by one of several test procedures.

DOT published a proposed rule on November 6, 1987 to reclassify chemicals consistent with United Nations (UN) International standards. The proposed flammable classifications are:

**Hazard Class 2.1** Gases, ignitable when in a mixture of 13 percent or less by volume with air, or have a flammable range with air of at least 12 percent regardless of the lower flammable limit. A gas is defined

as a substance with a normal boiling point of 20°C (68°F) or less at one atmosphere pressure. Flammable gases are not assigned to packing groups.

**Hazard Class 3** Liquids, with flash points of 60.5°C (141°F) or lower. Packing groups are assigned according to flash point and boiling point.

#### **Hazard Class 3 Packing Groups**

**Packing Group I** -- Boiling point less than 35°C (95°F).

**Packing Group II** -- Flash point less than 23°C (73°F) and boiling point greater than 35°C (95°F).

**Packing Group III** -- Flash point between 23°C (73°F) and 60.5°C (141°F) and boiling point greater than 35°C (95°F).

### **A.3 NFPA Classifications**

NFPA ratings for flammability are as follows (NFPA 1984):

- NFPA 4** Assigned to materials that will burn readily and are readily dispersed in air or will vaporize rapidly or completely at atmospheric pressure and normal ambient temperature. Gases and cryogenic materials are included, as well as liquids or liquefied gases with flash points below 22.8°C (73°F) and boiling points below 37.8°C (100°F).
- NFPA 3** Assigned to liquids and solids that can be ignited under almost all ambient temperature conditions. Liquids with flash points below 22.8°C (73°F) and boiling points at or above 37.8°C (100°F), or flash points at or above 22.8°C (73°F) and below 37.8°C (100°F).
- NFPA 2** Assigned to materials that must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur. Would not under normal conditions form hazardous atmospheres with air. Liquids with flash points greater than 37.8°C (100°F) and less than or equal to 93.4°C (200°F).
- NFPA 1** Assigned to materials that must be preheated before ignition can occur. Considerable preheating required under all ambient temperature conditions. Liquids, solids, and semi-solids with flash point greater than 93.4°C (200°F).
- NFPA 0** Assigned to materials that will not burn.

The classifications in NFPA 30 are:

- Flammable Liquid** Flash Point < 100°F (37.8°C)  
Vapor Pressure < 40 psia @ 100°F (37.8°C)
- Class IA** Flash Point < 73°F (22.8°C)  
Boiling Point < 100°F (37.8°C)
- Class IB** Flash Point < 73°F (22.8°C)  
Boiling Point ≥ 100°F (37.8°C)
- Class IC** Flash Point > 73°F (22.8°C) and < 100°F (37.8°C)

Combustible Liquid Flash Point  $\geq$  100°F (37.8°C)

Class II 100°F (37.8°C)  $\leq$  Flash Point < 140°F (60°C)

Class IIIA 140°F (60°C)  $\leq$  Flash Point < 200°F (93°C)

Class IIIB Flash Point  $>$  200°F (93°C)

NFPA 704 gives Class IA liquids a flammability rating of 4 and Class IB and IC liquids a flammability rating of 3.

#### A.4 EEC Indicative Criteria

The Indicative Criteria related to flammability are as follows (EEC 1982):

Flammable Gases:	Substances which in the gaseous state at normal pressure and mixed with air become flammable and the boiling point of which at normal pressure is 20°C or below.
Highly Flammable Liquids:	Substances which have a flash point lower than 21°C and the boiling point of which at normal pressure is above 20°C.
Flammable Liquids:	Substances which have a flash point lower than 55°C and which remain liquid under pressure, where particular processing conditions, such as high pressure and high temperature, may create major-accident hazards.

#### A.5 OSHA Regulations for Service Stations

Some of the specific requirements for flammable liquids (e.g., gasoline) included in OSHA's regulations for service stations are the following:

- Aboveground tanks in a bulk plant may be connected by piping to service station underground tanks if a valve is installed within control of service station personnel;
- Flammable liquids can be dispersed from tank vehicles in non-public areas if the vehicle, hose, and nozzle meet requirements;
- Class I (flammable) liquids cannot be stored in a basement or pit unless there is ventilation;
- Electrical and heating equipment must meet certain standards when installed in areas where flammable liquids are stored or handled;
- No smoking or open flames in areas used for fueling or servicing, and motors must be shut off during fueling.

## APPENDIX B

### METHODOLOGIES FOR MODELLING

#### B.1 WHAZAN (World Bank Hazard Analysis)

##### B.1.1 General Description

WHAZAN consists of a series of 13 consequence models (along with a database of chemical properties for a selection of important hazardous chemicals) which can be run individually or linked together. The consequence models consist of 4 release/evaporation models, 5 dispersion models, and 4 models dealing with fires and explosions. For this analysis, the linked model for instantaneous and prolonged releases was used. This model produces outputs which include pool fires, jet fires, vapor cloud explosions, fireballs/BLEVEs, evaporation rates for pools, and flashed fractions for liquified gases. The evaporation rate was input into the individual (stand-alone) vapor cloud dispersion model to determine the maximum distance to 50 percent of the LFL. Similarly, flashed fraction was input into the vapor cloud explosion stand-alone model to determine distances for vapor cloud explosions of liquified gases. The equations used in this report are described below. The models can be run on an IBM PC and most likely on other compatible systems.

##### B.1.2 WHAZAN Pressurized Release Outflow

For liquid stored in a refrigerated or pressurized container, WHAZAN calculates liquid outflow using the Bernoulli equation. The equation assumes the driving force for outflow may be the liquid head or difference between the storage pressure and the atmospheric pressure.

$$W = C_D A_R D_L [2(P_1 - P_A)/D_L + 2gH]^{1/2}$$

where:

W = release rate (kg/sec)  
C<sub>D</sub> = coefficient of discharge  
A<sub>R</sub> = area of release (m<sup>2</sup>)  
D<sub>L</sub> = density of the liquid (kg/m<sup>3</sup>)  
P<sub>1</sub> = initial (storage) pressure (N/m<sup>2</sup>)  
P<sub>A</sub> = atmospheric pressure (N/m<sup>2</sup>)  
g = gravitational acceleration (m/s<sup>2</sup>)  
H = liquid head (m)

The fraction of liquid that flashes once the fluid has reached atmospheric pressure is given by:

$$F_v = C_{PL}(T_1 - T_B)/H_{vap}$$

where:

F<sub>v</sub> = fraction flashed to vapor  
C<sub>PL</sub> = liquid specific heat (J/kg-K)  
T<sub>1</sub> = storage temperature (K)  
T<sub>B</sub> = boiling point (K)  
H<sub>vap</sub> = heat of evaporation (J/kg)

### B.1.3 WHAZAN Two-Phase Outflow

For a two-phase outflow (liquid and gas) of a flashing liquid, the release rate of the liquid is given by:

$$W = A_R C_D (2D_m(P_s - P_c))^{1/2}$$

where:

$$\begin{aligned} D_m &= \text{density of two-phase mixture (kg/m}^3\text{)} \\ P_s &= \text{saturated pressure (N/m}^2\text{)} \\ P_c &= \text{choked pressure (N/m}^2\text{)} \end{aligned}$$

The density of the 2-phase mixture at the exit plane is given by:

$$D_m = 1/(F_v/D_v) + (1-F_v)(D_L)$$

where:

$$D_v = \text{density of the vapor (kg/m}^3\text{)}$$

The fraction of the release that has flashed to vapor at the exit plane,  $F_v$ , is given by:

$$F_v = C_{PL}(T_1 - T_s)/H_{vap}$$

where:

$$\begin{aligned} C_{PL} &= \text{Liquid specific heat (J/kg-K)} \\ T_s &= \text{Saturation Temperature (K)} \end{aligned}$$

### B.1.4 WHAZAN Gas Outflow

These equations may be applied to the discharge of toxic and flammable gases from large vessels or pipes. This model assumes reversible adiabatic expansion and ideal gas behavior. To calculate gas outflow rates, WHAZAN uses the following:

$$W = Y C_D A_R P_1 [M G (2/(G+1))^{(G+1)/(G-1)} / R T]^{1/2}$$

where

$$\begin{aligned} W &= \text{gas outflow (kg/s)} \\ Y &= \text{coefficient in gas outflow model} \\ C_D &= \text{coefficient of discharge} \\ A_R &= \text{area of release (m}^2\text{)} \\ P_1 &= \text{initial (storage) pressure (N/m}^2\text{)} \\ M &= \text{molecular weight} \\ G &= \text{ratio of vapor specific heats at constant volume and at constant pressure} \\ R &= \text{universal gas constant (N-m/K-mole)} \\ T &= \text{temperature (K)} \end{aligned}$$

In most cases of interest, flow will be critical because upstream pressure exceeds:

$$P_A (2/(G+1))^{(G/(1-G))}$$

In these cases  $Y = 1.0$ . In the event that the upstream pressure is less than that given by the above expression, then:

$$Y = (P_A/P_1)^{1/G} [1 - (P_A/P_1)^{(G-1)/G}]^{1/2} [2((G+1)/2)^{(G+1)/(G-1)} / (G-1)]^{1/2}$$

### B.1.5 WHAZAN Adiabatic Expansion Outflow

These equations describe the initial behavior of an instantaneous pressurized release. The outflow may be used for subsequent dispersion calculations. The model assumes a core of uniform concentration containing 50% of the released mass surrounded by a peripheral zone characterized by a Gaussian distribution of concentration. For the estimation of the rapid adiabatic expansion experienced during the instantaneous release of a flashing liquid or pressurized vapor, WHAZAN uses a simple two zone hemispherical model. The expansion process is considered to have two stages:

- (1) In the first stage, gas expands down to atmospheric pressure or liquid flashes (as appropriate).

The change in internal energy is:

$$U_1 - U_2 = C_v(T_1 - T_2)$$

The energy of expansion is:

$$E = C_v(T_1 - T_2) \cdot P_A(V_2 - V_1)$$

where

$U_1$	=	initial internal energy (J/kg)
$U_2$	=	final internal energy (J/kg)
$C_v$	=	vapor specific heat at constant volume (J/kg-K)
$T_1$	=	storage temperature (K)
$T_2$	=	temperature after initial expansion (K)
$E$	=	energy of expansion (J)
$P_A$	=	atmospheric pressure (N/m <sup>2</sup> )
$V_1$	=	initial volume (m <sup>3</sup> )
$V_2$	=	final volume (m <sup>3</sup> )

- (2) In the second stage, the kinetic energy developed by the initial expansion drives the turbulent mixing of air into the cloud as the cloud spreads outward.

Once the expansion energy, E, has been determined, the expression for the turbulent coefficient is:

$$K_D = 0.0137 E^{1/2} V_{GO}^{1/3} [t E^{1/2} / V_{GO}^{1/3}]^{-1/4}$$

and the expression for the core radius as a function of time is:

$$r_c = 1.36(4K_D t)^{1/2}$$

where

$K_D$	=	turbulent diffusion coefficient (m <sup>2</sup> /sec)
$E$	=	expansion energy (J)
$V_{GO}$	=	volume of a unit gas at standard conditions (kg/m <sup>3</sup> )
$t$	=	time (sec)
$r_c$	=	radius of cloud core (m)

The equation for the concentration in the core is:

$$j_c = 0.0478 V_{GO} / ((4K_D t)^{3/2})$$

The following are expressions for the core concentration and radius at the end of the mixing:

$$j_c = 172.95E^{-0.9}$$

$$r_c = 0.08837E^{0.3}V_{GO}^{1/3}$$

It was found (Ulden 1974) that the end of the initial expansion occurred at a cloud radius,  $r$ , such that  $r/r_c = 1.456$ . At this value of  $r/r_c$ , 91% of the released material is still within the cloud.

#### B.1.6 WHAZAN Evaporation from Liquid Pool

For an instantaneous spill, if the atmospheric temperature is less than the normal boiling point of the liquid, evaporation is calculated by:

$$\frac{dm}{dt} = a(P_s M / RT_A) U^{(2-n)/(2+n)} r^{(4+n)/(2+n)}$$

where

$\frac{dm}{dt}$	=	change of mass with time (kg/sec)
$P_s$	=	saturated pressure (N/m <sup>2</sup> )
$M$	=	molecular weight
$R$	=	universal gas constant (N-m/K-mole)
$T_A$	=	atmospheric temperature (K)
$U$	=	wind speed at 10 m height (m/s)
$r$	=	radius of pool (m)
$a$	=	$4.785 \times 10^{-3}$ (neutral atmospheric stability)
$n$	=	0.25 (the midpoint of the observed range)

If the atmospheric temperature > normal boiling point of the chemical, two alternative models apply. If the dominant means of transfer of heat to the pool is wind, the previous equation is appropriate. If the dominant heat transfer mechanism is conduction through the ground, the appropriate model is as follows:

$$\frac{dm}{dt} = \pi r^2 k (T_A - T_B) / (H_{vap} t^{1/2})$$

where

$$k = 6.68 \times 10^5 \text{ to represent an average soil}$$

#### B.1.7 WHAZAN Pool Fires

To describe a pool fire phenomenon, WHAZAN uses equations governing pool spread and burning rate. In pool spread, the liquid is assumed to form a circular pool of uniform height. For an instantaneous spill, the pool radius is given by:

$$r = (t/8)^{1/2} \text{ (m)}$$

where:

$$\mathfrak{B} = (\pi D_L / 8 \text{ gm})^{1/2}$$

where:

$$\begin{aligned} D_L &= \text{density of liquid (kg/m}^3\text{)} \\ g &= \text{gravitational acceleration} = 9.8 \text{ m/s}^2 \\ m &= \text{released mass in cloud/pool (kg)} \end{aligned}$$

For continuous spills:

$$r = (t/\mathfrak{B})^{3/2}$$

where:

$$\mathfrak{B} = (9\pi D_L / 32gW)^{1/3}$$

To calculate burning rate for liquids having boiling points above ambient temperature:

$$\frac{dm}{dt} = \frac{0.001 H_c}{[C_{PL}(T_B - T_A) + H_{vap}]}$$

where:

$$\begin{aligned} H_c &= \text{heat of combustion (J/kg)} \\ C_{PL} &= \text{liquid specific heat (J/kg-K)} \\ H_{vap} &= \text{heat of evaporation (J/kg)} \\ T_B &= \text{boiling point (K)} \\ T_A &= \text{atmospheric temperature (K)} \\ dm/dt &= \text{pool spread (kg/sec)} \end{aligned}$$

For liquids having boiling points below ambient temperature:

$$\frac{dm}{dt} = \frac{0.001 H_c}{H_{vap}}$$

The heat released is calculated as:

$$Q = \frac{(\pi r^2 + 2\pi rH) \left(\frac{dm}{dt}\right) \eta H_c}{(72 \left(\frac{dm}{dt}\right)^{0.61} + 1)}$$



where:

$r$  = radius of pool (m)

The efficiency factor  $\eta$  has been shown by tests to have a value up to around 0.35.

The flame height is calculated as:

$$H = 84 r \left[ \frac{\left( \frac{dm}{dt} \right)}{D_A (2gr)^{1/2}} \right]^{0.61}$$

where:

$g$  = gravitational acceleration ( $m/s^2$ )

Numeric input data requirements for the "instantaneous" case are as follows:

<u>Parameter</u>	<u>Valid Range</u>	<u>Default</u>
Spill size	$10 - 10^7 kg$	-
Bund area	$0 - 10^6 m^2$	0
Ambient temperature	$200 - 400^\circ K$	$68^\circ F$
Efficiency factor	$0.01 - 1$	0.35

For the continuous case, the spill size is replaced by the spill rate and duration.

#### B.1.8 WHAZAN Jet Fires

The flame length is given by:

$$L = 18.5 W^{0.41}$$

where:

$W$  = release rate (kg/s)

$L$  = length (m)

This method should be applied when the release is of a flashing liquid. When the release is essentially gaseous, an alternative method is recommended. In this case, the flame length is based on the distance to the lower flammability limit (LFL) as given by the jet dispersion model. To calculate jet dispersion, the envelope within which the concentration of a turbulent jet is above a specified level,  $j_c$ , is represented by a major axis of length:

$$A = \left[ \frac{(b_1 + b_2)}{b_j j_c + D_{va} - 1} \right] D_j D_{v1}^{1/2} / (0.32 D_{va})$$

and a minor axis of length:

$$B = A \left[ - (1/b_2) \log_e \left[ \frac{\left( \frac{1 + j_c (1 - D_{va}) b_1}{(b_1 + b_2)} \right)}{2} \right] \right]^{1/2}$$

The shape parameters are given by

$$\begin{aligned} b_1 &= 50.5 + 48.2 D_{va} - 9.95 D_{va}^2 \\ b_2 &= 23.0 + 41.0 D_{va} \end{aligned}$$

where:

- $D_{va}$  = gas density at ambient conditions, relative to density of air ( $\text{kg/m}^3$ )
- $D_{v1}$  = gas density at stated conditions, relative to density of air ( $\text{kg/m}^3$ )
- $j_c$  = specified level of a turbulent jet - the envelope of concentrations of a turbulent jet is above this level ( $\text{kg/m}^3$ )
- $D_j$  = diameter of jet once expanded to atmospheric pressure (m), prior to entrainment of air

The jet shape is symmetrical about the major axis.  $D_j$  is calculated assuming adiabatic expansion.

#### B.1.9 WHAZAN Vapor Cloud Explosions (based on Buoyant Plume Dispersion)

WHAZAN model expresses vapor cloud explosions in terms of overpressure versus distance. Overpressurization is related to the dispersion concentration of the gas and assumptions about its explosive yield. WHAZAN uses the standard Gaussian model of plume dispersion to calculate the ground-level concentration of a buoyant release (where the release point can be at ground-level or at height, h):

$$C = W \exp \left( \frac{-y^2}{2\sigma_y^2} - \frac{h^2}{2\sigma_z^2} \right) \frac{1}{(U\sigma_y\sigma_z)}$$

where:

- $W$  = release rate ( $\text{kg/sec}$ )
- $y$  = crosswind distance (m)

$h$  = release height (m)

$U$  = wind speed at 10 m height (m/sec)

$\sigma_y \sigma_z$  = standard deviation of plume concentration profile in y and z directions

Then WHAZAN uses results of studies by Lees to relate the explosive yield of the gas concentration with the overpressurization waves distributed over distances. In addition, WHAZAN also presents results in terms of damage circles, using the Yellow Book methodology described in section B.3.2.

#### B.1.10 WHAZAN Fireballs/BLEVEs

WHAZAN uses empirical correlations to calculate the size, duration, and radiant intensity of fireballs of flammable liquid and/or vapor.

The maximum fireball radius is given by this model as:

$$r_m = 2.665 m^{.327}$$

where:

$m$  = released mass in cloud (kg)

and the duration by:

$$t = 1.089 m^{.327}$$

The energy released by combustion at efficiency is

$$Q = H_C m \eta$$

where:

$H_C$  = heat of combustion (J/kg)

$\eta$  = efficiency of combustion

where  $\eta$  is found to vary with the saturated vapor pressure of the material stored, as

$$\eta = 0.27 P_s^{.32}$$

where:

$P_s$  = saturated pressure (MN/m<sup>2</sup>)

The heat flux at a given distance from the fireball center is calculated assuming an inverse square-law relationship.

## B.2 ARCHIE (Automated Resource for Chemical Hazard Incident Evaluation)

### B.2.1 General Description

In a combined effort, FEMA, U.S. DOT, and U.S. EPA sponsored the development of a handbook and computer program entitled ARCHIE to provide emergency planning personnel with the tools necessary to evaluate the nature and magnitude of chemical release threats from potentially hazardous facilities.

A core part of the program estimates the downwind dispersion of a chemical release given a diversity of release scenarios. The program operates on an IBM personal computer or other compatible system. ARCHIE is capable of addressing a wide variety of common accident scenarios. The scenarios include nine methods to estimate discharge rate and duration of a gas or liquid release from a tank or pipeline, seven methods to estimate size of the liquid pool, two methods to estimate the rate at which a liquid pool will evaporate or boil, seven methods dealing with explosions and fires, and one method to estimate downwind chemical concentrations and hazard zones for the dispersion of vapor clouds.

### B.2.2 ARCHIE Pressurized Liquid Release

For a given liquid height and vapor space pressure, the instantaneous liquid release rate from a tank is given by the equation:

$$m = A_d C_d \sqrt{\rho_l [2g \rho_l (H_L - H_h) + 2(P_o - P_a)]}$$

where:

- $m$  = Discharge rate (kg/s)
- $g$  = Gravitational constant =  $9.8 \text{ m/s}^2$
- $\rho_l$  = Liquid density ( $\text{kg/m}^3$ )
- $P_o$  = Storage pressure ( $\text{N/m}^2$ )
- $P_a$  = Ambient pressure ( $\text{N/m}^2$ )
- $H_L$  = Liquid height above bottom of container (m)
- $H_h$  = Height of discharge opening (m)
- $A_d$  = Area of discharge opening ( $\text{m}^2$ )
- $C_d$  = Discharge coefficient

This assumes the tank is full. An average release rate for the tank at atmospheric pressure may be obtained by computing the time ( $T_e$ ) required to empty a tank. For a spherical tank:

$$T_e = \frac{16 D_T^{2.5}}{15 D_o^2 \sqrt{2g} C_d}$$

where:

- $D_T$  = Tank diameter (m)
- $D_o$  = Opening diameter (m)
- $T_e$  = Time to empty (sec)

The above equation assumes liquid is released through a circular opening at the bottom of the tank.

### B.2.3 ARCHIE Estimating Pool Size

Estimating pool areas that result from discharges of liquids is difficult and error-prone. Therefore, this model is composed of several methods that provide results that are approximate, but reasonable.

For non-boiling liquids, a pool area may be calculated based on user-supplied data from observations made at the potential accident site. The user may select use of the maximum credible pool area, or may choose a simple and very crude correlations based on experimental data, this being:

$$\log(A) = 0.492 \log(m) + 1.617$$

where:

m = total liquid mass spilled (lbs)

A = Pool area (ft<sup>2</sup>)

To compute pool areas for boiling liquids, one first needs to calculate the vaporization flux,  $E_v$ , which is then used in the pool spreading model. The vaporization flux is given as:

$$E_v = F\rho \left[ 92.6 \text{ EXP}(-0.0043T_b) \frac{M_w \times 10^{-7}}{6\beta} \right]$$

where:

$E_v$  = vaporization flux (kg/m<sup>2</sup>/sec)

$F = 0.5322 - 0.001035T_b$

$T_b$  = boiling point (°F)

$\rho$  = liquid density (kg/m<sup>3</sup>)

$M_w$  = molecular weight (kg/kmol)

$\beta$  = liquid specific gravity

This factor is used to determine the diameter of the pool fire.

Pool fire diameters can be calculated for continuous spills, where the spill continues at a specified finite rate for a long duration; instantaneous spills, which occur in a very short time; and finite duration spills, where a given volume of liquid is spilled over a given time interval. Pool fire diameters can also be calculated for surfaces with friction, and with no friction.

The maximum diameter of a pool is calculated for a sample scenario--an instantaneous release of a boiling liquid in the absence of friction:

$$D_{\max} = 1.7766 \left[ \frac{V^3 \Delta}{E_v^2} \right]^{1/8}$$

where:

$D_{\max}$  = maximum diameter of pool (m)

V = total liquid volume

$\Delta$  = effective gravity (same as gravitational constant, g, for spills) (m/sec<sup>2</sup>)

$E_v$  = vaporization flux (kg/m<sup>2</sup>/sec)

The time needed to reach the maximum diameter,  $t_{\max}$ , is given as:

$$t_{\max} = 0.6966 \left[ \frac{V}{\Delta E_v^2} \right]^{1/4}$$

#### B.2.4 ARCHIE Evaporation of Liquid Pool

Assuming the discharged liquid is near ambient temperature, a simplified model developed by the U.S. Air Force Engineering and Services Laboratory is used to predict the evaporation rate. The evaporative flux is given as:

$$E_v = 4.66 \times 10^{-6} U_w^{0.75} \frac{T_F P_s M_w}{P_{sh}}$$

where:

- $E_v$  = Evaporation flux (lbs/min/ft<sup>2</sup>)
- $U_w$  = Wind speed (miles/hr)
- $P_s$  = Vapor pressure of chemical (mm Hg)
- $P_{sh}$  = Vapor pressure of hydrazine (mm Hg)
- $M_w$  = Molecular weight of chemical
- $T_F$  = Spill temperature correction factor

The spill temperature correction factor is defined as follows:

$$\begin{aligned} T_F &= 1 \quad T_p < 0^\circ\text{C} \\ T_F &= 1 + 4.3 \times 10^{-3} T_p^2 \quad T_p > 0^\circ\text{C} \end{aligned}$$

where  $T_p$  is the pool temperature in degrees C. The vapor pressure of hydrazine is given by the following equation:

$$\ln(P) = 65.3319 - \frac{7245.2}{T} - 8.22 \ln(T) + 6.1557 \times 10^{-3} T$$

where T is in kelvins and P is in atmospheres.

Overall evaporation rate:

$$V_{ov} = E_v \cdot A$$

where

- $V_{ov}$  = evaporation rate (kg/s)
- $E_v$  = vaporization flux (kg/m<sup>2</sup>/s)
- $A$  = pool area (m<sup>2</sup>)

### B.2.5 ARCHIE Gas Discharge from Pressurized Vessel

For the gas discharge model, the initial rate from a pressurized vessel is also calculated. The model assumes that the process is adiabatic, and that wall friction is negligible. An expression for an instantaneous discharge rate under non-choked flow conditions is given as:

$$m = A_h \left( 2p_o \rho_o \frac{\gamma}{\gamma - 1} \left[ \left( \frac{p_1}{p_o} \right)^{2/\gamma} - \left( \frac{p_1}{p_o} \right)^{\frac{\gamma+1}{\gamma}} \right] \right)^{1/2}$$

Under choked flow conditions, the mass flow rate is calculated from:

$$m = A_h \left( \gamma p_o \rho_o \left( \frac{2}{\gamma + 1} \right)^{\frac{\gamma+1}{\gamma-1}} \right)^{1/2}$$

where:

- m = Discharge rate (kg/s)
- A<sub>h</sub> = Opening area (m<sup>2</sup>)
- γ = Ratio of specific heats
- p<sub>o</sub> = Tank pressure (Pascals)
- p<sub>1</sub> = Ambient pressure (Pascals)
- ρ<sub>o</sub> = Density (kg/m<sup>3</sup>)

This equation is based on ideal gas behavior.

### B.2.6 ARCHIE Vapor Cloud Fire Model

The purpose of this model is to estimate the dimensions of the downwind area that may be subjected to flammable and potentially explosive vapors and gases in the event of an accidental discharge. It applies both to toxic gases and vapor cloud fires. The model also estimates the maximum weight of flammable gas that may be airborne at any time. The size of the dispersion zone depends on the quantity of material released, its effective density, volatilization, prevailing atmospheric conditions, source elevation, and user-specified toxicity limit.

Either a neutrally buoyant or heavy gas model could be used to predict cloud dimensions. For neutrally buoyant gases, ARCHIE considers releases as point sources at ground level. The emission rate is constant. Ambient temperature was assumed to be 20°C. The model assumes steady state unless the release duration is significantly smaller than the characteristic downwind travel time. Relatively short-duration releases were assumed to be instantaneous. ARCHIE uses the finite duration model validated by Palazzi to predict gas dispersion. According to the model, the finite concentration (C<sub>f</sub>) at any location is given by:

$$C_f = \frac{C_c}{2} \left[ \operatorname{erf} \left( \frac{x}{(2)^{1/2} \sigma_x} \right) - \operatorname{erf} \left( \frac{x - U_w t}{(2)^{1/2} \sigma_x} \right) \right] \text{ when } t \leq t_R$$

$$C_f = \frac{C_c}{2} \left[ \operatorname{erf} \left( \frac{x - U_w(t - t_R)}{(2)^{1/2} \sigma_x} \right) - \operatorname{erf} \left( \frac{x - U_w t}{(2)^{1/2} \sigma_x} \right) \right] \text{ when } t \geq t_R$$

where:

$C_c$  = centerline concentration given as:

$$C_c = \frac{Q}{2\pi\sigma_y\sigma_zU_w} e^{-\frac{y^2}{2\sigma_y^2}} X \left[ \exp - \frac{(z-H)^2}{2\sigma_z^2} + \exp - \frac{(z+H)^2}{2\sigma_z^2} \right]$$

Here,  $t_R$  is the duration of release in seconds. The maximum concentration is given by the following equation:

$$C_{\max} = \frac{C_c}{2} \left[ \operatorname{erf} \left( \frac{x}{(2)^{1/2} \sigma_x} \right) - \operatorname{erf} \left( \frac{x - U_w t_R}{(2)^{1/2} \sigma_x} \right) \right], \quad x \leq \frac{U_w t_R}{2}$$

$$C_{\max} = \frac{C_c}{2} \left[ \operatorname{erf} \left( \frac{U_w t_R}{2(2)^{1/2} \sigma_x} \right) \right], \quad x \geq \frac{U_w t_R}{2}$$

The parameters used in the above equations are defined as follows:

- $C_{\max}$  = Maximum centerline concentration ( $\text{kg/m}^3$ )
- $Q$  = Continuous source release rate ( $\text{kg/sec}$ )
- $U_w$  = Wind speed ( $\text{m/sec}$ )
- $z$  = Vertical distance ( $\text{m}$ )
- $y$  = Crosswind distance ( $\text{m}$ )
- $x$  = Downwind distance ( $\text{m}$ )
- $H$  = Source height ( $\text{m}$ )
- $\sigma_x$  = Longitudinal standard deviation ( $\text{m}$ )
- $\sigma_y$  = Lateral standard deviation ( $\text{m}$ )
- $\sigma_z$  = Vertical standard deviation ( $\text{m}$ )

The dispersion distances for neutrally buoyant gases are generally 3 to 5 times larger than those for heavy gases.



### B.2.7 ARCHIE Unconfined Vapor Cloud Explosion

ARCHIE uses the TNT-equivalent model for use in evaluating the vapor cloud explosion scenario. The amount of combustion energy in the cloud is compared with the equivalent amount of TNT. Considering that only a fraction of the energy in the cloud will contribute to the explosion (this is known as the yield factor), and referring to the TNT explosion/overpressurization data, one can use the model to calculate the pressurization at distances from the explosion. The fraction of energy in the cloud assumed to contribute to the explosion ranges from 2 to 20 percent. Other simplifying assumptions include:

- Ambient temperature is 20°C;
- Effects of terrain, buildings, obstacles have not been considered.

The equation is stated as:

$$m_{TNT} = \left[ m_{cloud} \times \frac{\Delta H_c}{1155} \times Y_f \right]$$

where:

$m_{TNT}$  = TNT equivalent mass (lbs)  
 $\Delta H_c$  = Lower heat of combustion (kcal/kg)  
 $m_{cloud}$  = Mass in cloud (lbs)  
 $Y_f$  = Yield factor

Distance to a given overpressurization is then calculated from the equation:

$$X = m_{TNT}^{1/3} \exp \left( 3.5031 - 0.7241 \ln (O_p) + 0.0398 (\ln O_p)^2 \right)$$

where:

$X$  = distance to given overpressure (ft)  
 $O_p$  = Peak overpressure (psi)

### B.2.8 ARCHIE Tank Overpressurization Explosion Model

This model assumes that the pressurization waves created by an exploding tank will propagate omnidirectionally in a hemispherical field at ground level. The computational algorithm proceeds as follows:

1. Calculate the ratio  $P_i/P_a$  where  $P_a$  is the absolute ambient pressure and  $P_i$  is the absolute internal gas pressure at which the tank is expected to rupture.
2. Compute the ratio  $T_i/T_a$  where  $T_a$  is the absolute ambient air temperature and  $T_i$  is the absolute temperature of the gas in the tank.
3. Determine the initial overpressure ratio,  $P_{so}$ , by solving the following equation by trial and error:

$$f = 0 = \ln\left(\frac{P_i}{P_a}\right) - \ln(1 + P_{so}) - \frac{2\gamma_i}{1-\gamma_i} \ln \left[ 1 - \frac{(\gamma_i - 1)P_{so}}{2 \sqrt{\frac{T_i}{T_a}} \sqrt{\gamma_a^2 + 0.5\gamma_a(\gamma_a + 1)P_{so}}} \right]$$

where  $\gamma$  is the ratio of specific heat at constant pressure to that at constant volume.

4. Compute the nondimensional starting distance  $R_o$  from:

$$R_o = \frac{1}{\left[ \frac{4\pi}{3} \left( \frac{P_i}{P_a} - 1 \right) \right]^{1/3} \frac{\gamma_i - 1}}$$

5. Compute the value of  $R$  from:

$$R = \frac{r}{\left[ \frac{V \left( \frac{P_i}{P_a} - 1 \right)}{\gamma_i - 1} \right]^{1/3}}$$

where:

$V$  = Volume of the gas in the tank (ft<sup>3</sup>)

$r$  = Distance from the center of the tank at which the side-on overpressure is desired (ft)

6. Locate the point associated with  $P_{so}$  and  $R_o$  on an overpressurization graph.
7. Follow the nearest curve for  $P_s$  vs.  $R$  to the  $R$  value computed in step 5. Read the  $P_s$  value associated with this  $R$  value. If the gas vessel is on the ground and/or close to a reflecting surface, increase  $P_s$  by 100% for  $R$  less than 1 and by 10% for  $R$  greater than 1.
8. The side-on overpressure is determined by multiplying the above resultant value of  $P_s$  by the absolute value ambient atmospheric pressure  $P_a$ .

### B.2.9 ARCHIE Fireball Model

In calculating the maximum diameter and height the fireball attains, as well as the safe separation distances for fatality and injury, ARCHIE makes the following assumptions:

- Fuel is propane or has similar characteristics
- Ambient temperature is 20°C
- Atmospheric absorption of thermal radiation is negligible
- Fraction of combustion energy radiated = 0.2
- Observer is at ground level
- Minimum fatality zone is equal to half the maximum diameter calculated

Based on a series of experiments:

$$\begin{aligned}D_{\max} &= 16W^{1/3} \\Z &= 26.3W^{1/3} \\T &= 2.23W^{1/6}\end{aligned}$$

where:

W = Mass in vessel (lbs)  
D<sub>max</sub> = Maximum diameter of fireball (ft)  
Z = Maximum height of fireball (ft)  
T = Duration of fireball (s)

The safe separation distance for fatality, XF, in feet, was found to be:

$$\begin{aligned}XF &= 1.48W^{0.56} & W \geq 2000 \text{ lbs} \\XF &= 8.0W^{0.33} & W < 2000 \text{ lbs}\end{aligned}$$

For injury, the safe separation distance, XI, in feet, is:

$$XI = 4.53W^{0.52}$$

#### B.2.10 ARCHIE Liquid Pool Fire Model

ARCHIE calculates various pool fire factors to determine the radius in which injuries and fatalities are expected from the fire. These factors include burning velocity, maximum pool diameter, flame height, effective emissive power, incident flux, and view factor (fraction of flame seen by a given observer). In calculating these factors, there are several simplifying assumptions:

- Pool area is circular
- Observer is at ground level
- Ambient temperature is 20°C
- Atmospheric absorption of thermal radiation is negligible
- Negligible wind in the vicinity of the flame; thus, uniform thermal radiation field radially and no flame tilt
- Pool ignites shortly after release
- Burning rate equals spill rate

The scenario chosen to model is an instantaneous liquid hydrocarbon release in the absence of frictional resistance during spreading. The equation to estimate the burning velocity is:

$$y = \frac{92.6e^{-0.00437}, MW 10^{-7}}{\rho 6}$$

where:

$y$  = Burning velocity (m/s)  
 $MW$  = Molecular weight (kg/kmol)  
 $\rho$  = Liquid specific gravity  
 $T_B$  = Normal boiling point ( $^{\circ}F$ )

In the pool fire scenario, the radius of the pool increases until all the material is consumed by the fire. The maximum diameter and time to reach maximum diameter are given by:

$$D_{\max} = 1.7766 \left[ \frac{V^3 \Delta}{y^2} \right]^{1/8}$$

$$t_{\max} = 0.6966 \left[ \frac{V}{\Delta y^2} \right]^{1/4}$$

where:

$V$  = Total liquid volume ( $m^3$ )  
 $y$  = Burning velocity (m/s)  
 $\Delta$  = Effective gravity (same as gravitational constant ( $g$ ) for spills on land) ( $m/s^2$ )

The time averaged pool diameter is obtained by dividing the maximum diameter by the square root of two.

The mean visible flame height is based on equations correlated with data from laboratory fires. Visible flame height,  $H_{\text{flame}}$ , is expressed as:

$$H_{\text{flame}} = 42D_p \left[ \frac{BV\rho}{\rho_a \sqrt{gD_p}} \right]^{0.61}$$

where:

$H_{\text{flame}}$  = Flame height (m)  
 $\rho$  = Liquid density ( $kg/m^3$ )  
 $\rho_a$  = Air density at ambient temperature ( $kg/m^3$ )  
 $D_p$  = Pool diameter (m)  
 $g$  = Gravitational acceleration =  $9.8 m/s^2$

Effective emissive power of the flame accounts for the incident flux shielding by surrounding layers of smoke for liquid hydrocarbon fires. Based on literature data and correlated to the normal boiling point, effective emissive power is defined as:

$$E_p = -0.313 T_B + 117$$

where:

$$E_p = \text{Effective emissive power (kW/m}^2\text{)}$$
$$T_B = \text{Normal boiling point (}^\circ\text{F)}$$

The incident flux at any given location is given by the equation:

$$Q_{\text{incident}} = E_p \times \tau \times VF$$

where:

$$Q_{\text{incident}} = \text{Incident flux (kW/m}^2\text{)}$$
$$\tau = \text{Transmissivity}$$
$$VF = \text{Geometric view factor}$$

$\tau$ , the transmissivity coefficient, is mainly a function of the path-length (distance from observer to flame surface), relative humidity, and the flame temperature. For the calculation scheme in ARCHIE,  $\tau$  has been set to 1, and the attenuation of thermal flux due to atmospheric absorption is not taken into account. This assumption provides a conservative hazard estimate, since the presence of water and carbon dioxide tends to reduce the incident flux at any given location.

The view factor defines the fraction of flame that is seen by a given observer. This geometric term has been calculated as a function of distance from the flame center for an upright flame approximated by a cylinder. It has also been assumed that the optimum orientation between observer and flame that yields a maximum view factor prevails. The resulting equation is as follows:

$$VF = 1.143 \left[ \frac{R_p}{X} \right]^{1.757}$$

where:

$$X = \text{Distance from flame center (m)}$$
$$R_p = \text{Pool radius (m)}$$

For fatality, the incident flux level is set to 10 kW/m<sup>2</sup>. For injury, the corresponding level is 5 kW/m<sup>2</sup>. These levels are based on analysis of numerous sources of experimental burn data (Mudan, 1984). Applying these two damage criteria, the above equations were rearranged to solve for hazard distances  $X_{10}$  and  $X_{05}$  for fatality and injury, respectively:

$$X_{10} = 0.30 \frac{R_p}{0.3048} E_p^{0.57}$$

$$X_{05} = 0.43 \frac{R_p}{0.3048} E_p^{0.57}$$

where:

$X_{10}$  = Radius for expected fatalities (ft)

$X_{05}$  = Radius for expected injuries (ft)

### B.3 Yellow Book

#### B.3.1 General Description

The Yellow Book includes calculations for pool fires, vapor cloud fires, and vapor cloud explosions for gases; and pool fires and vapor cloud fires for liquids. For gases, two different methodologies are used for vapor cloud fires: the flash fraction of each gas is modeled as an instantaneous release and the non-flashed fraction is modeled as a continuous release from an evaporating pool. In both cases, dispersion as a neutrally buoyant cloud is assumed. The flash fraction of each gas is used to calculate the vapor cloud explosion results. Since there is no calculated flash fraction for liquids, no vapor cloud explosion results are calculated for liquids.

#### B.3.2 Vapor Cloud Explosion Calculations for Gases

Reference: Yellow Book, Chapter 4, "Spray Release," p. 44; Chapter 7, "Dispersion," pp. 25-27, and Appendix 2, p. 52; Chapter 8, "Vapor Cloud Explosion," pp. 24-25.

For gases, the flash fraction for a spray release is calculated. This fraction is then multiplied by the total quantity to obtain the quantity instantaneously in the air. The maximum fraction of this quantity that is between the upper and lower flammability limits is calculated. Damage circles for the resulting quantity can then be determined.

Equations:

Mass Flashed (Chapter 4, p. 44)

$$W_{\text{vap}} = X_{\text{vap},a} \cdot W_s$$

where

$W_{\text{vap}}$  = mass flashed (kg)

$X_{\text{vap},a}$  = weight fraction of vapor after expansion (flash fraction)

$W_s$  = mass stored (kg)

The flash fraction is calculated from the following equation (Chapter 4, p. 16, equation (3)):

$$X_{\text{vap},a} = X_{\text{vap},b} \frac{T_b}{T_1} + \frac{T_b C_1}{h_v} \cdot \ln \frac{T_1}{T_b}$$

where:

$X_{\text{vap},b}$  = weight fraction of vapor before expansion (assumed to be 0 for calculation of the flash fraction)

$T_b$  = boiling temperature of gas compressed to liquid (K)

$T_1$  = temperature of stored gas compressed to liquid (K)

$C_1$  = specific heat of gas compressed to liquid (J/kg-K)

$h_v$  = heat of evaporation of gas compressed to liquid (J/kg)

Flash fractions for selected gases are listed in Chapter 4, p.44, Table 1.

### B.3.2.1 Quantity of Vapor Contributing to Explosion (Chapter 7, pp. 25-26).

The equation in this section estimates the amount of gas in the explosive range. This amount develops as the dispersion progresses. Initially, and close to the source, the concentration in a large part of the cloud will be greater than the upper explosive limit;  $M_{ex}$  (the amount of gas in the explosive range) will then be small. As the dispersion progresses,  $M_{ex}$  increases to a maximum concentration that is reached when the maximum concentration is a little above the upper explosive limit. After this  $M_{ex}$  will gradually drop again.

$$\left(\frac{M_{ex}}{M}\right)_{\max} = \text{ERF}(\sqrt{v_2}) - \text{ERF}(\sqrt{v_1}) - \frac{2\sqrt{v_2}}{\sqrt{\pi}} \text{EXP}(-v_2) + \frac{2\sqrt{v_1}}{\sqrt{\pi}} \text{EXP}(-v_1)$$

where

$M_{ex}$  = amount of gas in explosive range (air not counted) (kg)

$M$  = total amount of gas which has escaped (kg)

$\text{ERF}(x)$  = error function =

$$\frac{2}{\sqrt{\pi}} \int_0^x \text{EXP}(-t^2) dt$$

(These values are listed in Appendix 2 on p 52.)

where

$$v = P_1/P_2, v_1 = [\text{Ln}(v)]/(v^2 - 1)$$

$$v_2 = \frac{v^2 \ln(v)}{v^2 - 1}$$

and

$P_1$  = upper explosive limit (UEL)

$P_2$  = lower explosive limit (LEL)

### B.3.2.2 Determination of Damage Circles (Chapter 8, p. 25)

For the limit value of certain types of damage(s) the relation is expressed below:

$$R(S) = C(S) \times (\eta E)^{1/3}$$



$R(S)$  = the radius of a damage circle (m)

$C(S)$  = constant for characteristic type of damage ( $\text{mJ}^{-1/3}$ )

A constant  $C(S)$  goes with each characteristic damage (S), listed on p.25. For glass damage causing injury,  $C(S) = .15$  (a corresponding overpressure is not given).

Only part of the total combustion energy in the explosive part of the cloud is available for shock wave propagation. This fraction is symbolized by the yield factor,  $\eta$ . This yield factor can be divided into two independent factors  $\eta_c$  and  $\eta_m$ , in which  $\eta = \eta_c \times \eta_m$ .  $\eta_c$  indicates the yield loss as a result of the non-stoichiometry of a cloud with a continuous development of fuel concentration in the explosive part of the cloud; it is put at 30%.  $\eta_m$  gives the mechanical yield of the combustion. Depending slightly on the type of gas,  $\eta_m$  is calculated as follows:

a. Isochoric combustion:  $\eta_m = \text{approx. } 33\%$

b. Isobaric combustion:  $\eta_m = \text{approx. } 18\%$

Where a gas cloud explosion occurs, there is probably some form of confinement which would result in isochoric combustion and a probable value for  $\eta_m$  of 33%.  $\eta$  would then equal approximately 10%.

To determine E, the energy content of the explosive part of the vapor cloud, an equation is given as an example on p. 26:

$$E = \text{mass} \times h_c$$

where

E = energy content (J)

$h_c$  = heat of combustion (J/kg)

mass = explosive part of vapor cloud (kg)

### B.3.3 Yellow Book Vapor Cloud Fire Calculations for Gases

Reference: Yellow Book, Chap. 5, "Evaporation," and Chap. 7, "Dispersion."

The evaporation rate for the pool left following the flash of an instantaneous release of a chemical is calculated using the following:

$$W_{\text{vap}} = \text{mass flashed}$$

The quantity remaining is:

$$W_{\text{pool}} = W_{\text{store}} - W_{\text{vap}}$$

where

$W_{\text{pool}}$  = mass in pool (kg)

$W_{\text{store}}$  = mass stored (kg)

The total volume of the chemical in the pool is calculated using the equation on page 42 of Chapter 5 in the Yellow Book:

$$V_{1,0} = \frac{W_1}{\rho_1}$$

where

$V_{1,0}$  = initial volume ( $m^3$ )  
 $W_1$  = mass in pool (kg)  
 $\rho_1$  = density ( $kg/m^3$ )

The pool of liquid will spread out until the minimum layer thickness is reached. The time,  $t_e$ , at which this takes place is best calculated using iterations of the equation on page 23:

$$V_{1,0} - \frac{8}{3} \times \left[ \frac{(\pi \times e^2 \times C'' \times g \times V_{1,0} \times t_e^3)}{\rho_1^2} \right]^{1/4} + \frac{16}{15} \times \pi \times C'' \times g \times \left( \frac{e}{\rho_1} \right) \times \delta_{1,min} \times t_e^{5/2} \\ - 2 \times (\pi \times C'' \times g \times V_{1,0} \times \delta_{1,min}^2 \times t_e^2)^{1/2} + \pi \times C'' \times g \times \delta_{1,min}^2 \times t_e^2 = 0$$

where

$V_{1,0}$  = volume of the spreading pool ( $m^3$ )  
 $e = \lambda_s \times (T_s - T_b) / h_v \times (\pi \times a_s)^{1/2}$  [p. 16] ( $kg/m^2 \cdot s^{1/2}$ )  
 $T_s$  = temperature of substrate  
 $T_b$  = boiling point of the liquid (K)  
 $a_s$  = thermal diffusivity of substrate =  $1.0 \times 10^{-6} m^2/s$  for concrete  
 $C''$  = constant for spreading liquids = 2  
 $g$  = acceleration due to gravity =  $9.8 m/s^2$   
 $t_e$  = time for minimum pool thickness to be attained (to be iterated) (s)  
 $\rho_1$  = density of the liquid ( $kg/m^3$ )  
 $\delta_{1,min}$  = minimum thickness = 0.01 m  
 $\lambda_s$  = coefficient of heat conduction of substrate = 1.1 W/m-K  
 $h_v$  = heat of evaporation of the liquid (J/kg)

This equation is used reiteratively to compute values of  $t_e$  until a minimum positive value is found.

The evaporation rate at the minimum pool thickness is calculated as follows:

$$M_p = 4 \times (\pi \times e^2 \times C'' \times g \times V_{1,0} \times t_e)^{1/2} - (8/3) \times \pi \times C'' \times g \times e \times \delta_{1,min} \times t_e^{3/2}$$

where

$M_p$  = the instantaneous evaporation rate at the minimum pool thickness ( $kg/m^2 \cdot s$ )

and all other variables are as defined above.

A dispersion distance to 50% of the lower flammability limit is calculated using the equation on page 15 of the Dispersion section of the Yellow Book (where y, z, and h all equal 0):

$$C(x,y,z) = \frac{M_p}{[2 \pi x U_w \sigma_y(x) \sigma_z(x)]}$$

where:

- $C(x, y, z)$  = concentration at coordinate x, y, z = 50% of LFL ( $\text{kg/m}^3$ )
- $M_p$  = evaporation rate at minimum pool thickness (as described above) ( $\text{kg/sec}$ )
- $\sigma_y(x)$  =  $ax^b = 0.128x^{0.905}$  (m)
- $\sigma_z(x)$  =  $cx^d = 0.2x^{0.76}$  (m)  
(using values in the table on page 10 for neutral conditions)
- $U_w$  = wind speed at 10 m height (m/sec)

#### B.3.4 Vapor Cloud Fire Calculations for Gases (Based on Fraction Flash, 50% LFL)

Reference: Yellow Book, Chapter 4, "Spray Release," pp. 36, 44; Chapter 7, "Dispersion," p. 23.

The following equations estimate the consequence distance for a vapor cloud fire for gases, assuming that a percentage of the total amount released is immediately vaporized; this vaporized quantity is assumed to be available for the vapor cloud fire. The quantity evaporating from the pool that remains after flashing is not considered in this calculation.

The flashed mass is calculated as follows (Chapter 4, p 16):

$$W_f = X_{\text{vap,a}} \cdot W_s$$

$W_f$  = mass flashed (kg)

$X_{\text{vap,a}}$  = flash fraction (see Section B.3.2 for calculation)

$W_s$  = mass stored (kg)

The quantity  $W_f$  is then used as an instantaneous source using equation 23 (p. 24 in "Dispersion" section), where the concentration at a point (x, y, z) at time t is given as:

$$C(x,y,z,t) = \frac{m}{(2 \pi)^{3/2} \sigma_{xI} \sigma_{yI} \sigma_{zI}} \exp \left[ -\frac{(x - U_w t)^2}{2 \sigma_{xI}^2} \right] \exp \left[ -\frac{y^2}{2 \sigma_{yI}^2} \right]$$

$$\left[ \exp \left[ -\frac{(z-h)^2}{2 \sigma_{zI}^2} \right] + \exp \left[ -\frac{(z+h)^2}{2 \sigma_{zI}^2} \right] \right]$$

where:

$m$  = source strength for an instantaneous release (kg)

$x$  = coordinate in wind direction (m)

$y$  = coordinate at right angles to wind direction (m)

$z$  = coordinate in vertical direction (m)

$U_w$  = wind speed at 10 m height (m/s)

$h$  = source height (m)

$\sigma_{xI}$   $\sigma_{yI}$   $\sigma_{zI}$  = standard deviations in x, y, and z directions for an instantaneous source

We assume that  $y$ ,  $z$ , and  $h = 0$ , and that  $x = U_w t$ , where  $U_w$  is wind speed, to determine the distance the cloud has traveled in the x direction only:

$$C(x,0,0,t) = \frac{m}{(2\pi)^{3/2} \sigma_{xI} \sigma_{yI} \sigma_{zI}}$$

From p. 23,  $\sigma_{xI}$ ,  $\sigma_{yI}$ , and  $\sigma_{zI}$  are described by these equations:

$$\sigma_{xI} = e_1 x^{f_1}$$

$$\sigma_{yI} = a_1 x^{b_1}$$

$$\sigma_{zI} = c_1 x^{d_1}$$

where  $a_1$ ,  $b_1$ ,  $c_1$ ,  $d_1$ ,  $e_1$ , and  $f_1$  are constants

From page 24:

$$e_1 = .13 \quad f_1 = 1$$

$$a_1 = a/2 \quad b_1 = b$$

$$c_1 = c \quad d_1 = d$$

From Table 10 on page 10,  $a = .128$ ,  $b = .905$ ,  $c = .20$ .

Therefore:

$$\sigma_{xI} = .13 x$$

$$\sigma_{yI} = .064 x^{.905}$$

$$\sigma_{zI} = .2 x^{.76}$$

$C$  = concentration

$$m = W_s$$

$$C = \frac{W_s}{(2\pi)^{3/2} (.064)(.2)(.13) x^{2.665}}$$

Solve for x:

$$x = \left[ \frac{W_s}{(2\pi)^{3/2} (.13)(.064)(.13)C} \right]^{1/2.665} = \left[ \frac{m}{.01703C} \right]^{0.375}$$

### B.3.5 Pool Fire Calculations for Gases and Liquids

Reference: Chapter 4, "Spray Release," p. 44; Chapter 6, "Heat Radiation," pp. 8-14, 19-35.

To determine the heat radiation into the environment, the radiating surface (the flame from the burning pool) is seen as an upright cylinder with diameter D and length L. The radiation load q per unit area exposed which is experienced at a distance r from the center of the fire is (Ch. 6, p. 8):

$$q_r = \tau_1 \times F \times E$$

where

- $q_r$  = radiation load per unit area at a distance r from the center of the fire (kW/m<sup>2</sup>)
- $\tau_1$  = atmospheric coefficient of transmission
- F = geometric view factor
- E = average intensity of radiation (kW/m<sup>2</sup>)

#### B.3.5.1 Atmospheric Coefficient of Transmission

Part of the radiated heat is absorbed by the air between the object exposed to radiation and the fire. This reduction is taken into account by  $\tau_1$ , the coefficient of transmission. The size of this coefficient is dependent upon the amount of water vapor between the flame and the object, the air temperature, and the relevant distance (r) between the object and the center of the fire.

The relevant distance (r) is the unknown variable for the purposes of this study.  $q_r$ , the radiation load, is assumed to be 12.5 kw/m<sup>2</sup>, the intensity that corresponds to one percent probability of fatality for a 30 second exposure. Figure 2 on p. 35 gives  $\tau_1$  as a function of the product of vapor pressure and relevant distance. The vapor pressure is determined by multiplying the relative humidity by the saturated vapor pressure (given in Table 1, p.19) at a prevailing temperature. To be conservative, a value of 10 percent was used for relative humidity.

To estimate the relevant distance, an iterative process, including calculations and estimates of  $\tau_1$  (atmospheric coefficient of transmission) and F (geometric view factor) from B.3.5.1, B.3.5.2, and B.3.5.3, was used. Assuming a relevant distance and multiplying that estimate by the vapor pressure yields an estimate for t, using the table on page 35. This value for t can then be used in calculating the view factor (F), as described in B.3.5.2 and B.3.5.3. The estimate for F is used to determine another estimate for the relevant distance. This new assumed distance is used to estimate another value for t, and the steps above are reiterated. This reiterative process is used until the relevant distance approaches a single value.

#### B.3.5.2 The Geometric View Factor F

The effect of the geometrical shape of the flame and the place and orientation of the exposed object are incorporated in the view factor F. The size of the view factor is determined by the length to diameter ratio of the flame (Chapter 6, p. 9).

$$\frac{L_f}{d} = 42 \left[ \frac{m''}{\rho_a \sqrt{g \cdot d}} \right]^{.61}$$

where

$L_f$  = length of the flame (m)  
 $d$  = diameter of the flame (m)  
 $m''$  = rate of evaporation (kg/m<sup>2</sup>s)  
 $g$  = acceleration due to gravity = 9.8 m/s<sup>2</sup>  
 $\rho_a$  = density of air (at 18°C = 1.213 kg/m<sup>3</sup>)

The diameter of the flame is assumed equal to the diameter of the pool. The diameter of the pool is calculated from the volume of propane in the pool, assuming the pool spreads out to a thickness of .01 m.

The calculation for the rate of evaporation ( $m''$ ) is dependent upon whether the stored material is a liquid with a boiling point below the ambient temperature or above the ambient temperature.

Liquids with a boiling point below ambient temperature are gases stored under high pressure conditions. The equation is given in Chapter 6, p. 10:

$$m'' = \frac{h_c}{h_v} \cdot 10^{-3} \text{ kg/m}^2\text{sec}$$

where

$h_c$  = heat of combustion (J/kg)  
 $h_v$  = heat of vaporization (J/kg)

For liquids with a boiling point above ambient temperature (Ch. 6, p.11):

$$m'' = \frac{h_c}{C_p \Delta T + h_v} \cdot 10^{-3}$$

where

$C_p$  = specific heat or heat capacity at constant pressure (J/kg.K)  
 $\Delta T$  = boiling temperature - ambient temperature (K)

The value of the view factor (not the size) can be determined by solving the initial equation for radiation load for F:

$$\begin{aligned} q_r &= \tau_1 \times F \times E \\ F &= q_r / (\tau_1 \times E) \end{aligned}$$

### B.3.5.3 Intensity of Radiation of the Fire

The value for E, the average intensity of radiation ( $\text{W/m}^2$ ), is dependent on both the type of fuel and on the diameter of the pool. The magnitude of the average intensity of radiation is given on Table 3, p. 21 for four gases: butane, propane, ethylene, and propylene. The value for the other substances is calculated using the equation in Chapter 6, Appendix 2, p. 32 for liquids with a boiling point above ambient temperature:

$$E = \frac{0.35 \left[ \frac{h_c}{C_p \Delta T + h_v} \cdot 10^3 \right] h_c}{72 \left[ \frac{h_c}{C_p \Delta T + h_v} \cdot 10^3 \right]^{.61} + 1}$$

where

E = radiation intensity ( $\text{W/m}^2$ )

$h_c$  = heat of combustion ( $\text{J/kg}$ )

$C_p$  = heat capacity ( $\text{J/kg-K}$ )

$h_v$  = heat of vaporization ( $\text{J/kg}$ )

$\Delta T$  = boiling point - ambient temperature ( $^{\circ}\text{K}$ )

The length to diameter ratio can then be determined using the equation in Chapter 6, p. 9:

$$\frac{L_f}{d} = 42 \left[ \frac{m''}{\rho_a \sqrt{g \cdot d}} \right]^{.61}$$

Table 1 on p. 24 gives view factors between a vertical upright cylinder and a surface on the ground. The table lists the view factors as coordinates between the ratio of flame length to radius and the ratio of the distance of the object from the fire to radius. These ratios are diagrammed in Appendix I. Using the section of the table that gives maximum view factors, the ratio a/b is assumed to be the length to radius ratio and is taken to be twice the flame length to diameter ratio. Using the known ratio a/b and the view factor F, the ratio c/b can be estimated and the relevant distance (c) to the object receiving radiation can be determined. Using this new assumed distance, a new value for  $\tau_1$  can be estimated in a reiteration of the process, until the distance approaches a single value.

### B.3.6 Vapor Cloud Fire for Liquids (Dispersion Distance to 50% LFL)

Reference: Yellow Book, Chapter 5, "Evaporation," Pp. 29-38; Chapter 7, "Dispersion," Pp. 15-16.

The calculations in this section model the consequence distance in a vapor cloud fire when the material evaporates from a pool on the ground rather than flashing into a vapor state after an instantaneous release. The consequence distance to a concentration that is 50% of the lower flammability limit (LFL) is modeled. The 50% LFL figure is a conservative level that accounts for uncertainties like the uneven dispersion within the cloud and the estimated value of the lower flammability limit. To determine the mass flux of evaporating non-boiling liquids, the following equation is used (Chapter 5, P. 33):

$$\dot{m}_{nb}'' = 2.10^{-3} U_{w,10}^{0.78} r_{pool,c}^{-0.11} \frac{M}{RT_{nb}} (P_w - P_{\infty}) \text{ for: } P_w < 2 \times 10^4 \text{ Pa}$$

where

- $\dot{m}_{nb}$  = evaporation rate of non-boiling liquids (kg/m<sup>2</sup>s)
- $U_{w,10}$  = wind speed at 10 meters = 3 m/s
- $r_{pool,c}$  = radius of confined liquid pool = 46.8 in
- $M$  = molecular weight (kg/kmol)
- $R$  = molar gas constant =  $8.3 \times 10^3$  (J/kmol-K)
- $T_{nb}$  = temperature of non-boiling liquid = ambient temperature = 293 K
- $P_w$  = partial vapor pressure on liquid surface (Pa)
- $P_{\infty}$  = partial vapor pressure in surroundings = 0 for liquid (Pa)

In order to calculate the dispersion to 50% LFL, the equation for the concentration for a continuous source on p. 15 of Chapter 7 is used:

$$C(x,y,z) = \frac{\dot{m}}{2\pi U_w(x) \sigma_y(x) \sigma_z(x)} \text{EXP} \left( -\frac{y^2}{2\sigma_y^2(x)} \right) \cdot \left[ \text{EXP} \left( -\frac{(z-h)^2}{2\sigma_z^2(x)} \right) + \text{EXP} \left( -\frac{(z+h)^2}{2\sigma_z^2(x)} \right) \right]$$

with y, z, and h = 0, this equation reduces to:

$$C(x) = \frac{\dot{m}}{2\pi U_w \sigma_y(x) \sigma_z(x)}$$

where

$C(x)$  = concentration as a function of x only (kg.m<sup>-3</sup>)

$\dot{m}$  = source strength (kg.s<sup>-1</sup>)

$U_w$  = wind speed at 10 m height (m/s)

$h$  = source height (m)

$\sigma_y(x) = ax^b$  and  $\sigma_z(x) = cx^d$ ,

(see p. 10 for practical formulae for  $\sigma_y$  and  $\sigma_z$ )

To calculate  $\dot{m}$ , the source strength, we multiply  $\dot{m}_{nb}$  (kg/m<sup>2</sup> sec) the mass flux of the evaporating liquid, by the area of the pool (m<sup>2</sup>). The equation is then solved for x, the distance to the 50% LFL concentration.



## B.4 AIChE-Sponsored Course Materials

### B.4.1 General Description

The American Institute of Chemical Engineers (AIChE) course material includes calculations for pool fires and vapor cloud fires for gases and liquids. For vapor cloud fires for gases, the flash fraction of each gas is modeled as an instantaneous release; the AIChE material explains that the consequence distance produced by the initial flash fraction cloud is so much larger than the consequence distance for the remaining non-flashed part that it dominates in assessing the hazard area. The calculations for vapor cloud explosions and BLEVES appear incomplete and cannot be used as methodologies.

### B.4.2 Vapor Cloud Fire Calculation for Gases

Reference: AIChE Pp. B-65 and B-85; D-9 - D-10.

The fraction of liquified gas vaporized ( $v$ ) is given on p. D-9:

$v$  = fraction of liquid vaporized

$$v = 1 - \exp\{C_p/h_v(T_b - T_1)\}$$

where

$C_p$  = specific heat (Btu/lb°F)  
 $h_v$  = latent heat of vaporization (Btu/lb)  
 $T_b$  = normal boiling point (°F)  
 $T_1$  = temperature of liquid stream (°F)

We then multiply the fraction of the liquid vaporized by the quantity released to determine the amount of vaporized material ( $Q$ ).

To determine the distance to 50% LFL, the equation on p. B-84 is used:

$$X_{(x,y,z,t)} = \frac{2Q}{\pi^{3/2} C^3 (Ut)^{3/2-n/2}} \exp \left[ - \frac{(Ut)^{n-2} x^2 + y^2 + z^2}{C^2} \right]$$

$$X_{(0,0,0,t)} = 131Q/(Ut)^{2.62} \text{ for neutral conditions}$$

where

$X_{(0,0,0,t)}$  = concentration at the center of the cloud (assume 50% LFL) at time  $t$  (kg/m<sup>3</sup>)  
 $U$  = wind speed (m/s)  
 $t$  = time (s)  
 $Ut$  = distance (m)

The equation is solved for  $Ut$ , the distance, by including the 50% LFL concentration as  $X$  and the quantity of vaporized material,  $Q$ .

#### B.4.3 Vapor Cloud Fire Calculations for Liquids

Reference: AIChE Pp. D-2 - D-5, D-9 - D-10.

To determine the rate of evaporation from a circular pool, the area of the pool must first be determined. This is calculated by dividing the total volume of liquid by the thickness of the pool, which is estimated for different surface types in Table I on p. D-4. The radius of the pool is then determined and used in the following equation for evaporation (p. D-2):

$$E = K' U^{(2-n)/(2+n)} r^{(4+n)/(2+n)} \text{ (kg/sec)}$$

where

$$K' = a' \mu_o D^{2n/(2+n)} z_1^{-n/(2+n)}$$

$$\mu_o = \frac{P_s M}{RT} = \text{vapor density (kg/m}^3\text{)}$$

$$P_s = \text{saturated vapor pressure (N/m}^2\text{)}$$

$$M = \text{molecular weight (kg/kmol)}$$

$$R = \text{universal gas constant (8314.3 J/mol K)}$$

$$T = \text{ambient temperature, K}$$

$$D = \text{vapor diffusivity value}$$

Values of  $n$ ,  $a'$ ,  $K'/U_o$  are given in Table II (using neutral stability).

The distance that a vapor cloud disperses from a liquid pool is given by the equation on p. D-9:

$$d_1 = \{(36.8)(Q)/(U)(C_L)\}^{0.552} \text{ (m)}$$

where

$$d_1 = \text{distance at which cloud is diluted to LFL (m)}$$

$$Q = \text{source strength or volumetric vapor escape rate (m}^3\text{/sec)}$$

$$U = \text{wind velocity (m/sec)}$$

$$C_L = \text{lower explosion limit (vol}_{\text{vapor}}\text{/vol}_{\text{air}}\text{)} \\ \text{(used 50\% LEL versus LEL)}$$

The volumetric vapor escape rate ( $Q$ ) is calculated from the Evaporation rate using the Ideal Gas Law. The evaporation rate (kg/s) is converted to moles using the molecular weight, moles are converted to liters at the prevailing temperature, and liters may then be converted to  $\text{m}^3$ .

#### B.4.4 Pool Fire Calculations for Liquid and Gases

Reference: AIChE Pp. D-16 - D-29.

The AIChE methodology does not distinguish between liquids and gases in the calculation of the thermal flux at a specified distance from a burning pool. To determine the liquid burning rate ( $v$ ), the following equation is used (P. D-17):

$$v = v_o \{1 - \exp(-k_1 d)\} \text{ (for a pool of diameter } d\text{)}$$

where

$$-k_1 = \text{attenuation coefficient}$$

$$v = \text{liquid burning rate (lbs/s)}$$

$$\begin{aligned}v_{\infty} &= \text{liquid burning rate of infinite pool} = .0030 h_c/h'_v \text{ (in/min)} \\d &= \text{pool diameter (ft)} \\h_c &= \text{heat of combustion (Btu/lb)} \\h'_v &= \text{sensible heat of vaporization (Btu/lb) = sensible heat + latent heat}\end{aligned}$$

The mass burning rate can then be calculated (p. D-17):

$$M = v\rho$$

where

$$\begin{aligned}M &= \text{mass burning rate (lb/ft}^2 \text{ sec)} \\v &= \text{liquid burning rate (in/min)} \\\rho &= \text{density of the liquid (lb/ft}^3 \text{)}\end{aligned}$$

The mass burning rate is then used to estimate the ratio of flame height (h) to pool diameter (d) (p. D-18):

$$\frac{h}{d} = 42 \left[ \frac{m}{\rho_a (gd)^5} \right]^{.61}$$

where

$$\begin{aligned}m &= \text{mass burning rate (kg/m}^2 \text{-sec)} \\\rho_a &= \text{density of ambient air (1.206 kg/m}^3 \text{)} \\g &= \text{acceleration of gravity = 9.78 m/sec}^2 \\d &= \text{pool diameter (m)}\end{aligned}$$

Thermal flux is calculated by dividing the total heat (Q) by the surface area of the flame envelope (S). Total heat available during the pool fire is:

$$Q = (h_c)(m)(A) \quad (\text{Btu/sec})$$

where

$$\begin{aligned}h_c &= \text{heat of combustion (Btu/lb)} \\m &= \text{mass burning rate (lb/ft}^2 \text{-sec)} \\A &= \text{pool area (ft}^2 \text{)}\end{aligned}$$

Pool area is determined by dividing the total volume of the liquid by the thickness of the pool. Thicknesses for spreading pools over different surfaces are listed in Table I, page D-4.

Only a fraction of the total heat is radiated from the surface of the flame envelope. These fractions may be read from Table II, page D-5. The surface heat flux ( $q_o$ ) can then be determined (p. D-19).

$$q_o = Q/S \quad (\text{Btu/ft}^2 \text{ hr})$$

where

$$\begin{aligned}S &= \text{surface area of cylindrical flame envelope} = 2\pi rh + \pi r^2 \text{ (ft}^2 \text{)} \\Q &= \text{total heat (Btu/hr)}\end{aligned}$$

The heat absorbed ( $q_r$ ) by a receiver at various distances ( $x$ ) from the pool center is given by (p. D-19):

$$q_x = \epsilon_r \tau_x F_x q_o$$

where

- $q_o$  = heat flux at flame surface (Btu/ft<sup>2</sup> hr)
- $\epsilon_r$  = receiver surface absorptivity (from Table III, D-25 - assumed to be 1, all heat absorbed)
- $\tau_x$  = atmospheric transmissivity at distance  $X = 1 - \epsilon_w$
- $F_x$  = view factor from receiver to flame
- $\epsilon_w$  = emissivity of water in air

The atmospheric transmissivity is estimated as a function of distance ( $x$ ) from the center of the flame to the receiver times the partial pressure of water.  $\epsilon_w$  is read from a graph of emissivity versus the partial pressure of water (atm) times the distance (ft) found on p. D-26, assuming the partial pressure is .0024 for worst case winter conditions.

The view factor ( $F$ ) is read from tables on pp. D-27 - D-29. It is plotted as a function of distance ( $D$ ) from the flame centerline to the receiver flame radius and the plots are arranged by the flame height/pool diameter ratio.

The distance is initially assumed to find a value for  $E_w$ , and  $q_x$  is equal to 12.5 kw/m<sup>2</sup>. The equation is then solved for  $F_x$ , and the distance "D" can be determined. Successive approximations of the calculations for the value of  $F_x$  are then calculated using the new values for the distance until one value is approached.

## B.5 Green Book

The Technical Guidance for Hazards Analysis ("Green Book") contains calculations for the consequence distances for Vapor Cloud Fires, where 50% of the lower flammability limit (LFL) or another fraction of the LFL may be used as concentration level.

Reference: Green Book, Appendix G, "Equations Used for Estimation of Vulnerable Zones."

The rate of release of a chemical is needed for calculation of the distance for a specific concentration. It is dependent on the quantity of chemical released, the nature of the release scenario (i.e., pool of liquid), and the properties of the chemical released. For spilled pools of chemicals, the rate of release is usually taken to be the evaporation rate (rate of volatilization). Using the assumptions presented above; the following equation is used to calculate the rate of release to air for liquids (in lbs/min):

$$QR = \frac{(60 \text{ sec/min} \times MW \times K \times A \times VP \times (929 \text{ cm}^2/\text{ft}^2))}{R \times (T1 + 273) \times (760 \text{ mmHg/atm}) \times 454 \text{ g/lb}}$$

where

- QR = rate of release to air (lbs/min)
- MW = molecular weight (g/g mole)
- K = gas phase mass transfer coefficient (cm/sec)
- A = surface area of spilled material (ft<sup>2</sup>)
- VP = vapor pressure of material at temperature T1 (mm Hg)
- R = 82.05 atm cm<sup>3</sup>/g mole K
- T1 = temperature at which the chemical is stored (°C)

The equation for the evaporation rate (rate of volatilization) can be rewritten as follows:

$$QR = \frac{0.162 \times MW \times K \times A \times VP}{R(T1 + 273)}$$

K can be estimated based on a known value for a reference compound as follows:

$$K = K_{\text{ref}} \times (MW_{\text{ref}}/MW)^{1/3}$$

Using water as the reference compound:

$$K_{\text{ref}} = K_{\text{water}} = 0.25 \times (U)^{0.78}$$

where: U = windspeed (m/sec)

Combining the two equations above:

$$K = 0.25 (U)^{0.78} \times (18/MW)^{1/3}$$

Combining equations for QR and K yields the following equations (Green Book p. G-2):

$$QR = \frac{0.162 \times 0.25 \times (U)^{0.78} \times (18)^{1/3} \times MW^{2/3} \times A \times VP}{R \times (Tl + 273)}$$

$$QR = \frac{0.106 \times (U)^{0.78} \times MW^{2/3} \times A \times VP}{R \times (Tl + 273)}$$

Calculation of the surface area (A) of the spilled material is carried out as described below.

The following assumptions are used to calculate the surface area of the spill:

Density = 62.4 lb/ft<sup>3</sup> (i.e., all liquids are assumed to have the same density as water)  
Depth of pool is 0.033 ft (1 cm)

The surface area of the spilled liquid (ft<sup>2</sup>) is (Green Book p. G-3):

$$A = \frac{QS \text{ (lbs)}}{62.4 \text{ lb/ft}^3 \times 0.033 \text{ ft}} = 0.49 \times QS$$

where

QS = quantity spilled (lbs)  
A = surface area (ft<sup>2</sup>)

Substituting for A in the above equation for release rate, the quantity released to air per minute (QR) can be estimated as follows:

$$QR = \frac{0.106 \times (U)^{0.78} \times MW^{2/3} \times 0.49 \times QS \times VP}{82.05 \times (Tl + 273)}$$

For gases, it is assumed (Green Book p. 3-3) that the entire mass is released in the ten minutes:

$$QR = \frac{QS \text{ (lbs)}}{10 \text{ minutes}}$$

where

QS = quantity spilled (lbs)  
QR = rate of release to air (lbs/min)

The following equation was used to derive the distance to a concentration (C). The concentration downwind of a release is given by (Green Book p. G-4):

$$C = \frac{QR}{\pi \sigma_y \sigma_z U}$$

for a ground level release with no effective plume rise where:

C	=	airborne concentration (g/m <sup>3</sup> ) (assumed 50% LFL)
QR	=	rate of release to air (g/sec)
$\pi$	=	3.141
$\sigma_y \times \sigma_z$	=	dispersion deviation, horizontal (y), and vertical (z)
U	=	windspeed (m/sec)

This equation is then solved for the product  $\sigma_y \sigma_z$ , the dispersion deviation.

$$\sigma_y \sigma_z = \frac{QR}{\pi U(50\% \text{ LFL})}$$

To determine the downwind distance (d), Exhibit G-1 on p. G-6 lists  $\sigma_y$  and  $\sigma_z$  as functions of d, using the stability category D for open-country conditions:

$$\sigma_y = .08 d (1 + .0001 d)^{-1/2}$$

$$\sigma_z = .06 d (1 + .0015 d)^{-1/2}$$

$$d = \text{downwind distance, for } 10^2 < d < 10^4 \text{ (m)}$$

However, the product of  $\sigma_y$  and  $\sigma_z$  derived from the downwind concentration equation cannot be used to solve the product of  $\sigma_y$  (d) and  $\sigma_z$  (d). The value from these successive approximations was then compared to the numerical value of the  $\sigma_y \sigma_z$  product from the concentration equation to estimate the distance (d).

## APPENDIX C

### HAZARD CRITERIA

#### C.1 Explosion Overpressure

##### C.1.1 Damage and Injury from Blast Waves

Blast waves from accidental explosions can cause damage to people and property by subjecting them to transient crushing pressures and winds. Relatively simple concepts have been used to quite effectively correlate blast wave properties with damage. The concept states that damage is primarily a function of either the peak overpressure, the impulse or some combination of these factors. Peak overpressure is most commonly used.

Criteria for peak overpressures causing personal injury are given in Exhibit C-1, including injury from direct blast effects and from flying glass. Guidelines for peak overpressures required to produce property damage are presented in Exhibit C-2. These data are largely based on empirical observations. There seems to be general agreement between sources on the data presented in Exhibit C-2; however, the same is not true for the data presented in Exhibit C-1. According to Exhibit C-1, lung damage may occur at overpressures of 10 psi. According to other sources, threshold lung damage may not occur until peak overpressures reach 30 to 40 psi (Grelecki, Richmond 1968). The values for corresponding fatalities also vary. According to the Exhibit, the lowest overpressure cited for fatality from direct blast effects is 14.5 psi. According to another source, a 1% mortality rate is probable at 27.0 psi. Others cite values in the range of 35 to 120 psi as the threshold overpressure value for fatalities, 20.5 to 180 psi for a 50% fatality rate, and 29 to 250 psi for a 99% fatality rate (Grelecki, Richmond 1968, Lees 1980).

Exhibits C-3 and C-4 show how lethality and injury vary with both overpressure and the duration of the blast wave. Exhibit C-5 shows similar data as a function of both pounds of TNT and range in feet.

Exhibits C-3 through C-5 present potential injury levels resulting from direct exposure to blast overpressures in an open area. They do not take into account injuries resulting from property damage presented in Exhibit C-2. For example, substantial injury and possible deaths may result from the shattering of concrete walls at 2.0 to 3.0 psi. In planning with regard to injury to personnel, the following guidelines have been recommended (Brasie and Simpson 1968):

- Personnel in areas subject to overpressures greater than about 2 psi are likely casualties from fragmentation or self-impact against objects.
- Personnel beyond the under 1 psi overpressure range should be reasonably safe inside a reinforced structure away from windows or, if outdoors, lying on the ground.

Nazario (1988) recommends that all personnel in open terrain be evacuated if the potential of 0.3 psi overpressure exists and recommends evacuating personnel in buildings that might experience an overpressure exceeding 1.0 psi (0.25 psi overpressure if the building has windows).

According to the AIChE (1987), the usual procedure for control room design for plants where there may be the potential for explosions is to design the control room for a peak overpressure on the order of 1 to 3 psi.



**EXHIBIT C-1. HUMAN INJURY CRITERIA**  
(Includes Injury from Flying Glass and Direct Overpressure Effects)

Overpressure (psi)	Injury	Comments	Source
0.6	Threshold for injury from flying glass*	Based on studies using sheep and dogs	(Fletcher, Richmond, and Yelverton 1980)
1.0 - 2.0	Threshold for skin laceration from flying glass	Based on Army data	(Lees 1980)
1.5	Threshold for multiple skin penetrations from flying glass (bare skin)*	Based on studies using sheep and dogs	(Fletcher, Richmond, and Yelverton 1980)
2.0 - 3.0	Threshold for serious wounds from flying glass	Based on Army data	(Lees 1980)
2.4	Threshold for eardrum rupture	Conflicting data on eardrum rupture	(Lees 1980)
2.8	10% probability of eardrum rupture	Conflicting data on eardrum rupture	(Lees 1980)
3.0	Overpressure will hurl a person to the ground	One source suggested an overpressure of 1.0 psi for this effect	(Brasie and Simpson 1968)
3.4	1% eardrum rupture	Not a serious lesion	(U.S. DOT 1988)
4.0 - 5.0	Serious wounds from flying glass near 50% probability	Based on Army data	(Lees 1980)
5.8	Threshold for body-wall penetration from flying glass (bare skin)*	Based on studies using sheep and dogs	(Fletcher, Richmond, and Yelverton 1980)
6.3	50% probability of eardrum rupture	Conflicting data on eardrum rupture	(Lees 1980)

\* Interpretation of tables of data presented in reference.

**EXHIBIT C-1. HUMAN INJURY CRITERIA**  
(Includes Injury from Flying Glass and Direct Overpressure Effects)  
(continued)

Overpressure (psi)	Injury	Comments	Source
7.0 - 8.0	Serious wounds from flying glass near 100% probability	Based on Army data	(Lees 1980)
10.0	Threshold lung hemorrhage	Not a serious lesion (applies to a blast of long duration (over 50 msec); 20-30 psi required for 3 msec duration waves)	(U.S. DOT 1988)
14.5	Fatality threshold for direct blast effects	Fatality primarily from lung hemorrhage	(Lees 1980)
16.0	50% eardrum rupture	Some of the ear injuries would be severe	(U.S. DOT 1988)
17.5	10% probability of fatality from direct blast effects	Conflicting data on mortality	(Lees 1980)
20.5	50% probability of fatality from direct blast effects	Conflicting data on mortality	(Lees 1980)
25.5	90% probability of fatality from direct blast effects	Conflicting data on mortality	(Lees 1980)
27.0	1% Mortality	A high incidence of severe lung injuries (applies to a blast of long duration (over 50 msec); 60-70 psi required for 3 msec duration waves)	(U.S. DOT 1988)
29.0	99% probability of fatality from direct blast effects	Conflicting data on mortality	(Lees 1980)

EXHIBIT C-2. PROPERTY DAMAGE CRITERIA

Overpressure (psi)	Damage	Source(s)
0.03	Occasional breaking of large glass windows already under strain	(Lees 1980)
0.04	Loud noise (143dB). Sonic boom glass failure	(Lees 1980)
0.10	Breakage of windows, small, under strain	(Lees 1980)
0.15	Typical pressure for glass failure	(Lees 1980)
0.30	"Safe distance" (probability 0.95 no serious damage beyond this value). Missile limit. Some damage to house ceilings. 10% window glass broken.	(Lees 1980)
0.4	Minor structural damage	(McRae 1984, Lees 1980)
0.5 - 1.0	Shattering of glass windows, occasional damage to window frames. One source reported glass failure at 0.147 psi	(Brasie and Simpson 1968, Air Force 1983, U.S. DOT 1988, Lees 1980)
0.7	Minor damage to house structures	(Lees 1980)
1.0	Partial demolition of houses, made uninhabitable	(Lees 1980)
1.0 - 2.0	Shattering of corrugated asbestos siding Failure of corrugated aluminum/steel paneling Failure of wood siding panels (standard housing construction)	(Brasie and Simpson 1968, Air Force 1983, U.S. DOT 1988, Lees 1980)
1.3	Steel frame of clad building slightly distorted	(Lees 1980)
2.0	Partial collapse of walls and roofs of houses	(Lees 1980)

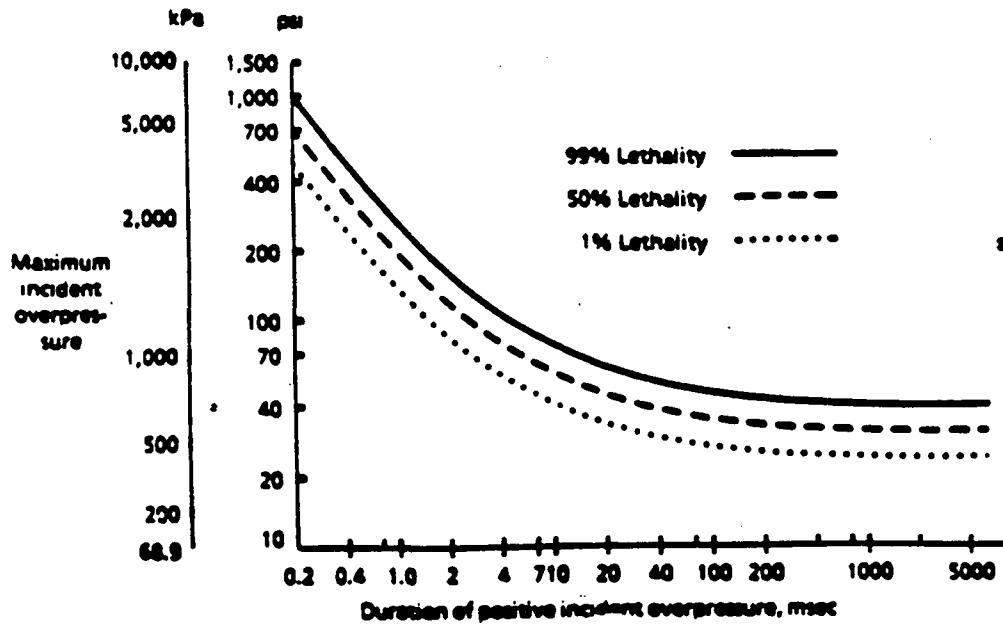
**EXHIBIT C-2. PROPERTY DAMAGE CRITERIA**  
(continued)

Overpressure (psi)	Damage	Source(s)
2.0 - 3.0	Shattering of non-reinforced concrete or cinder block wall panels (1.5 psi according to another source)	(Brasie and Simpson 1968, Air Force 1983, U.S. DOT 1988, Lees 1980)
2.3	Lower limit of serious structural damage	(Lees 1980)
2.5	50% destruction of brickwork of house	(Lees 1980)
3.0	Steel frame building distorted and pulled away from foundations	(Lees 1980)
3.0 - 4.0	Collapse of self-framing steel panel buildings Rupture of oil storage tanks Snapping failure - wooden utility tanks	(Brasie and Simpson 1968, U.S. DOT 1988, Lees 1980)
4.0	Cladding of light industrial buildings ruptured	(Lees 1980)
4.8	Failure of reinforced concrete structures	(McRae 1984)
5.0	Snapping failure - wooden utility poles	(Brasie and Simpson 1968, Lees 1980)
5.0 - 7.0	Nearly complete destruction of houses	(Lees 1980)
7.0	Loaded train wagons overturned	(Lees 1980)
7.0 - 8.0	Shearing/flexure failure of brick wall panels (8-12 inches thick, not reinforced)	(Brasie and Simpson 1968, Air Force 1983, U.S. DOT 1988, Lees 1980)
	Sides blown in of steel frame buildings	(Air Force 1983)
	Overturning of loaded rail cars	(Brasie and Simpson 1968, U.S. DOT 1988)

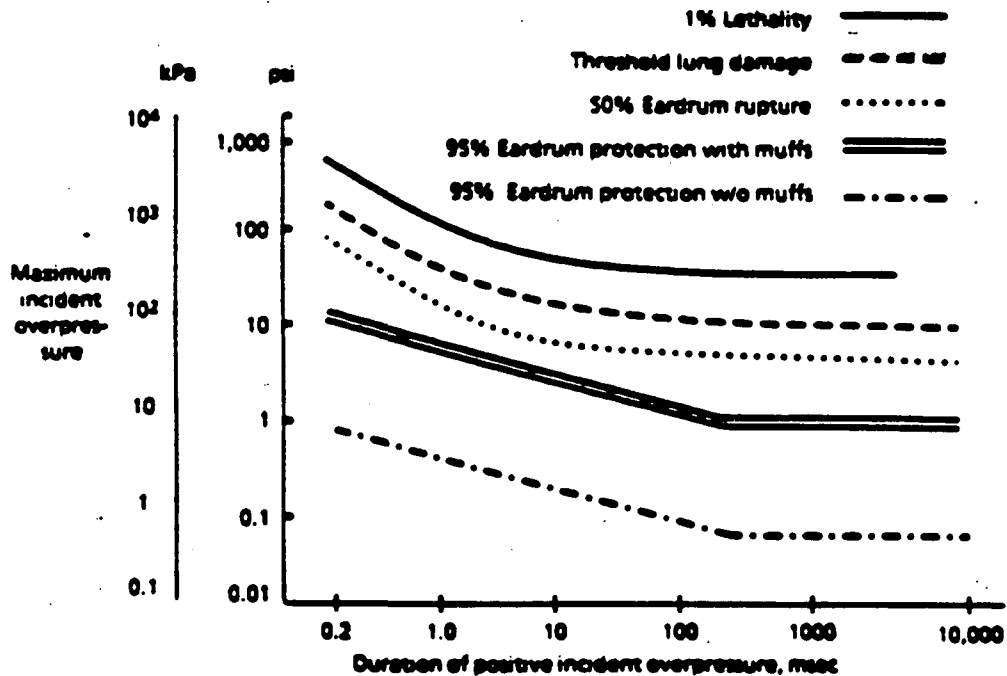
**EXHIBIT C-2. PROPERTY DAMAGE CRITERIA**  
(continued)

Overpressure (psi)	Damage	Source(s)
9.0	Loaded train box-cars completely demolished	(Lees 1980)
10.0	Probable total destruction of buildings	(Lees 1980)
30.0	Steel towers blown down	(Brasie and Simpson 1968, Air Force 1983)
88.0	Crater damage	(McRae 1984)

**EXHIBIT C-3. LETHALITY CURVES**  
(For a 154 lb Person in Free Stream Situations)



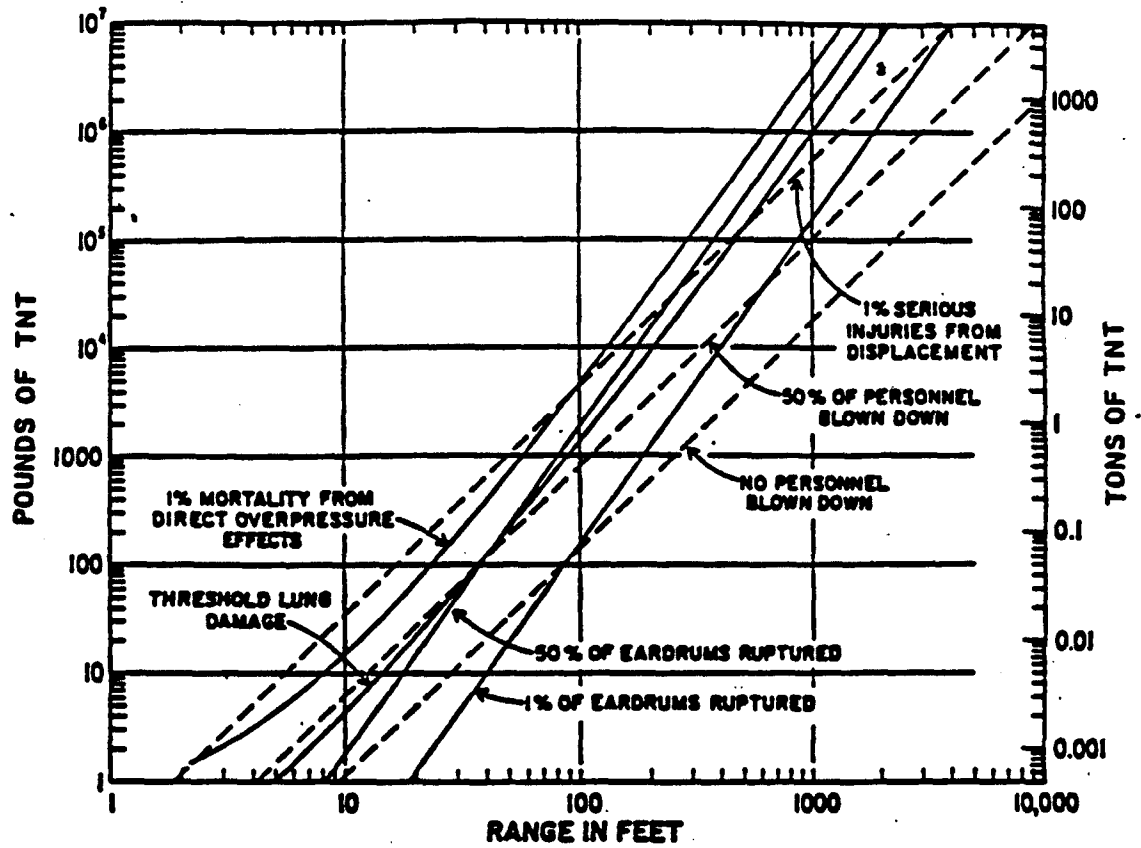
**EXHIBIT C-4. LETHALITY AND INJURY CURVES**  
(For a 154 lb Person in Free Stream Situations)



Notes: msec = milliseconds  
kPa = kilopascals = 6.895 psi  
psi = pounds per square inch = 0.1450 kPa

Source: U.S. DOT 1988, Kokinakis and Rudolph 1982.

**EXHIBIT C-5. AIR-BLAST CRITERIA FOR PERSONNEL STANDING IN THE OPEN**



Source: U.S. DOT 1988, Richmond and Fletcher 1971.

Note that although glass is reported to shatter at an overpressure level of 0.5 psi (see Exhibit C-2), there is evidence that human injury from flying glass is unlikely at this level. Lees (1980) cites a report stating that risk of injury from flying window glass is negligible for an explosion that gives a peak overpressure of 0.6 psi or less. Lees also cites a report giving the skin laceration threshold for flying glass as 1-2 psi and the serious wound threshold as 2-3 psi (see Exhibit C-1). Fletcher, Richmond, and Yelverton (1980) carried out experiments on the effects on sheep and dogs of glass fragments from windows shattered by various blast overpressures. Their results (briefly cited in Exhibit C-1) appear to agree reasonably well with the data reported by Lees. Their data indicate that the threshold for injury from flying glass is about 0.6 psi. Multiple injuries from skin penetration (i.e., ten or more) may occur for bare skin at overpressures of 1.5 psi or higher. Flying glass may penetrate the body-wall at 5.8 psi or higher if the skin is bare. The authors point out that the skin and body-wall thickness of men and sheep are approximately the same (Fletcher, Richmond, and Yelverton 1980); therefore, the data reported should be roughly applicable to humans.

#### **C.1.2 Distance Determination for Different Overpressures**

To determine the effect on distance of modeling to different overpressures for vapor cloud explosion, the WHAZAN model was run for several different overpressures for vapor cloud explosions of ethylene and propylene. Exhibit C-6 shows explosion overpressure versus consequence distance for 100,000 pound releases of ethylene and propylene. The curves are not linear; a relatively small change in overpressure at the lower end of the scale results in a relatively large change in the consequence distance, while a relatively small change in overpressure at the upper end of the scale results in relatively small change in consequence distance. However, increasing the overpressure at the upper end of the overpressure scale appears to have a much smaller effect on the consequence distance.

#### **C.2 Flammability Limits**

As noted in the text (Section 8.2), the lower flammable limit (LFL) of a vapor or gas is the minimum concentration in air that will ignite and propagate flame. Using 50 percent of the LFL to estimate consequence distances for vapor cloud fires accounts for variability within the cloud from its edge to its center and inaccuracies in dispersion modeling.

To determine the effect of using different concentrations to estimate the consequence distance for vapor cloud fires, two representative chemicals, ethylene and propylene, were modeled using WHAZAN at 10,000 pounds and 100,000 pounds. Moderate meteorology (wind speed 3.0 meters per second and atmospheric stability D) was assumed. The model was run for three concentrations, at 50% of the lower flammable limit, at the lower flammable limit, and at 200% of the lower flammable limit. The results of modeling are shown graphically in Exhibit C-7. The results curves for both quantities and both chemicals modeled are basically similar in shape but of differing magnitudes. The results curves clearly are not linear: the change in magnitude between the consequence distance obtained at 50% of the lower flammable limit and that at the lower flammable limit is clearly greater than the change between the lower flammable limit and 200% of the lower flammable limit for all four curves.



Exhibit C-6  
HAZARD CRITERIA COMPARISON FOR VAPOR CLOUD EXPLOSIONS  
FOR INSTANTANEOUS RELEASES OF 100,000 POUNDS

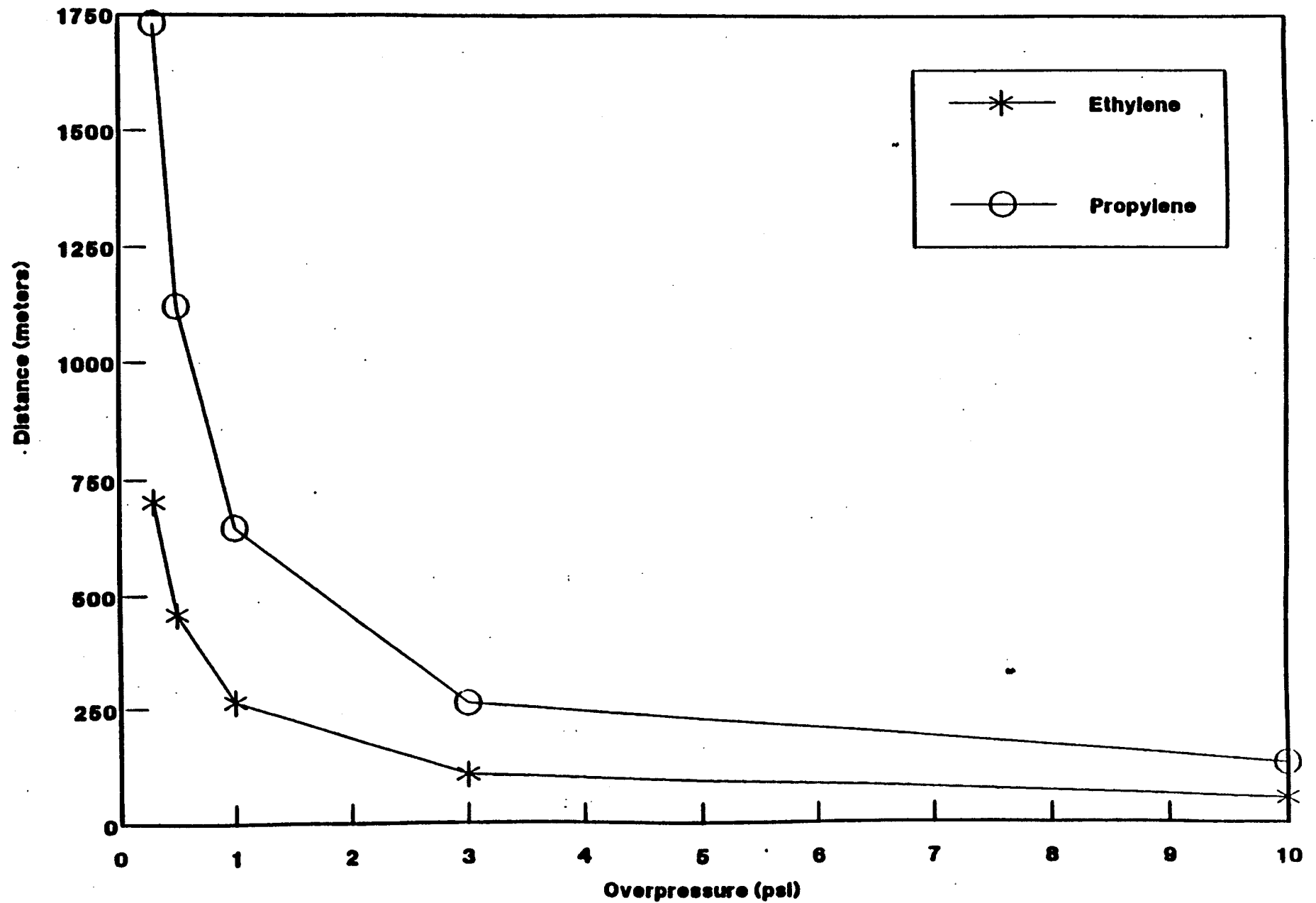
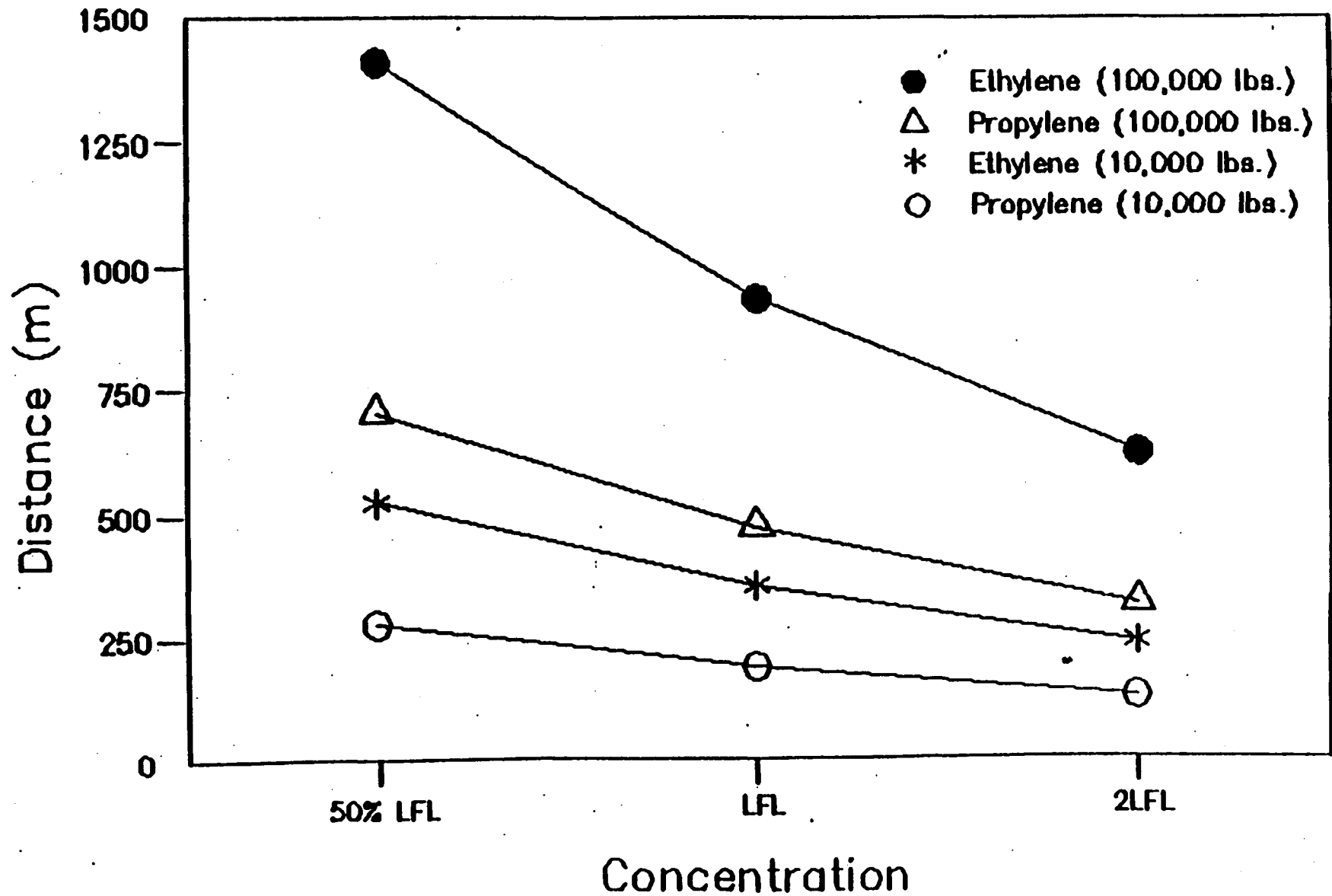


Exhibit C-7  
**HAZARD CRITERIA COMPARISON FOR VAPOR CLOUD FIRES**  
**FOR EVAPORATING POOLS FROM INSTANTANEOUS RELEASES, MODERATE METEOROLOGY**  
(Wind speed 3.0 meters per second, atmospheric stability class D)



### C.3 Heat Radiation

#### C.3.1 Heat Radiation Levels Causing Death and Injury

Human injury or fatality from heat radiation from fires is likely to occur as a result of direct exposure to a fire rather than as a result of property damage caused by a fire. The extent of the injury caused by heat radiation depends both on the heat level and the time of exposure. Exhibit C-8 presents heat radiation levels and exposure times required to produce various human effects or injuries. There are few data on fatalities from heat radiation; the fatality data shown in Exhibit C-8 have been calculated or estimated. Both the WHAZAN (1988) and Mudan (1984) fatality data appear to be based on data on the relation between thermal radiation intensity and burn injury for nuclear explosions at different yields (Eisenberg et al. 1975, as cited by Mudan 1984). According to Mudan (1984), exposure times for nuclear explosions are typically very short and interpretation of the data is "somewhat subjective."

In a review of fire hazards by Takata in 1970 for the Armed Services Explosive Safety Board, estimates are presented of critical radiant exposure necessary to ignite or damage several types of targets, including people. As reported in Vol. I of the CPIA "Hazards of Rockets and Propellants," minimum critical exposures necessary to ignite or damage people range from 94.6 kW/m<sup>2</sup> for a 10-second exposure time to 35.1 kW/m<sup>2</sup> for a 60-second exposure and 27.8 kW/m<sup>2</sup> for a 190-second exposure.

The WHAZAN manual includes a table for fatality based upon exposure to heat. Exhibit C-9 presents the lethality of heat flux as presented in the manual.

The exposure times given for the fatality levels are calculated from a Probit equation (indicating statistical probability based on deviations from the mean of normal distribution), as follows:

$$\text{Probit} = -14.9 + 2.56 \log_e (t \times Q^{4/3} \times 10^{-4})$$

where Q is in watts per square meter and t is in seconds

The WHAZAN model uses radiation levels of 12.5 to 37.5 kW/m<sup>2</sup> in its output, based on the likelihood that people would be able to "shelter" from the fire within 30 seconds to one minute. For this period of time, the probability of fatality ranges from 1 percent at 12.5 kW/m<sup>2</sup> for 30 seconds to 99 percent at 37.5 for 50 seconds (see Exhibit C-9).

Mudan (1984) estimated a slightly lower fatality threshold of 10 kW/m<sup>2</sup> for a 40-second exposure time. Mudan estimated this level from the data of Eisenberg et al (1975, as cited by Mudan 1984). A plot of thermal radiation versus time for injuries and fatalities shows that 1 percent fatalities may occur at 10 kW/m<sup>2</sup> at a time of 40 seconds. The 10 kW/m<sup>2</sup> radiation level suggested by Mudan, which is used in the ARCHIE model to determine the zone for fatalities from pool fires, agrees quite well with the 12.5 kW/m<sup>2</sup> level.

Nazario (1988) indicates that all personnel should be evacuated from areas where the radiant heat is likely to exceed one-half of the threshold value for second degree burns to bare skin (5,000 Btu/hr-ft<sup>2</sup>, or 16 kW/m<sup>2</sup>, for an exposure of about 5 seconds).

EXHIBIT C-8

HUMAN INJURY CRITERIA  
(Thermal Radiation Effects on Bare Skin)

<u>Thermal Radiation (kW/m<sup>2</sup>)</u>	<u>Time of Exposure (Seconds)</u>	<u>Injury or Effect</u>	<u>Source</u>
1.75	60	Pain threshold reached	WHAZAN 1988 Buettner 1951 Hardy et al. 1953 Stoll and Greene 1959 Bigelow et al. 1945
3	27 92	Severe pain Second degree burn	HCHAP 1989
5	15 13 40	Pain threshold reached "Unbearable" pain Second degree burn (injury threshold)	WHAZAN 1988 Mudan 1984 Mudan 1984
6.4	8 20	Pain threshold reached Second degree burn	WHAZAN 1988 WHAZAN 1988
10	40	Fatality threshold	Mudan 1984
12.5	30 80 200	1% fatality 50% fatality 99% fatality	WHAZAN 1988 WHAZAN 1988 WHAZAN 1988
37.5	8 20 50	1% fatality 50% fatality 99% fatality	WHAZAN 1988 WHAZAN 1988 WHAZAN 1988

Exhibit C-9

**FATALITY FROM HEAT EXPOSURE**

Thermal Radiation (kW/m <sup>2</sup> )	Seconds exposure for % fatality		
	1%	50%	99%
1.6	500	1300	3200
4.0	150	370	930
12.5	30	80	200
37.5	8	20	50

Reference: WHAZAN Handbook (1988)

### **C.3.2 Distance Determination for Different Heat Radiation Levels**

Modeling was carried out using the WHAZAN model to determine the effect of heat radiation level on consequence distances for BLEVEs and pool fires.

#### **C.3.2.1 BLEVES**

For BLEVEs, ethylene and propylene were modeled at 10,000 pounds and 100,000 pounds. The model was run for three heat flux consequence levels, 4 kW/m<sup>2</sup>, 12.5 kW/m<sup>2</sup>, and 37.5 kW/m<sup>2</sup>. The relationship between the consequence distance results for ethylene and propylene and other hydrocarbon results for BLEVEs can be seen by examining Exhibit C-10. The results curves for both quantities and both hydrocarbons modeled are basically similar in shape but of differing magnitudes. The results curves clearly are not linear: the change in magnitude between the consequence distance obtained at 4 kW/m<sup>2</sup> and that at 12.5 kW/m<sup>2</sup> is clearly greater than the change between 12.5 kW/m<sup>2</sup> and 37.5 kW/m<sup>2</sup> for all four curves. Results for other hydrocarbons studied are approximately the same as the results for propylene.

#### **C.3.2.2 Pool Fires**

For pool fires, ethylene and propylene were modeled at 10,000 pounds and 100,000 pounds. The WHAZAN model was run for three heat flux consequence levels, 1.6 kW/m<sup>2</sup>, 4 kW/m<sup>2</sup>, and 12.5 kW/m<sup>2</sup>. Modeling results are presented in Exhibit C-11. The results curves for both quantities and both chemicals modeled are basically similar in shape but of only slightly differing magnitudes. The results curves clearly are not linear: the change in magnitude between the consequence distance obtained at 1.6 kW/m<sup>2</sup> and that at 4 kW/m<sup>2</sup> is clearly greater than the change between 4 kW/m<sup>2</sup> and 12.5 kW/m<sup>2</sup> for all four curves. Results for other hydrocarbons studied are approximately the same as the results for ethylene and propylene.

Exhibit C-10  
HAZARD CRITERIA COMPARISON FOR BLEVES,  
INSTANTANEOUS RELEASES

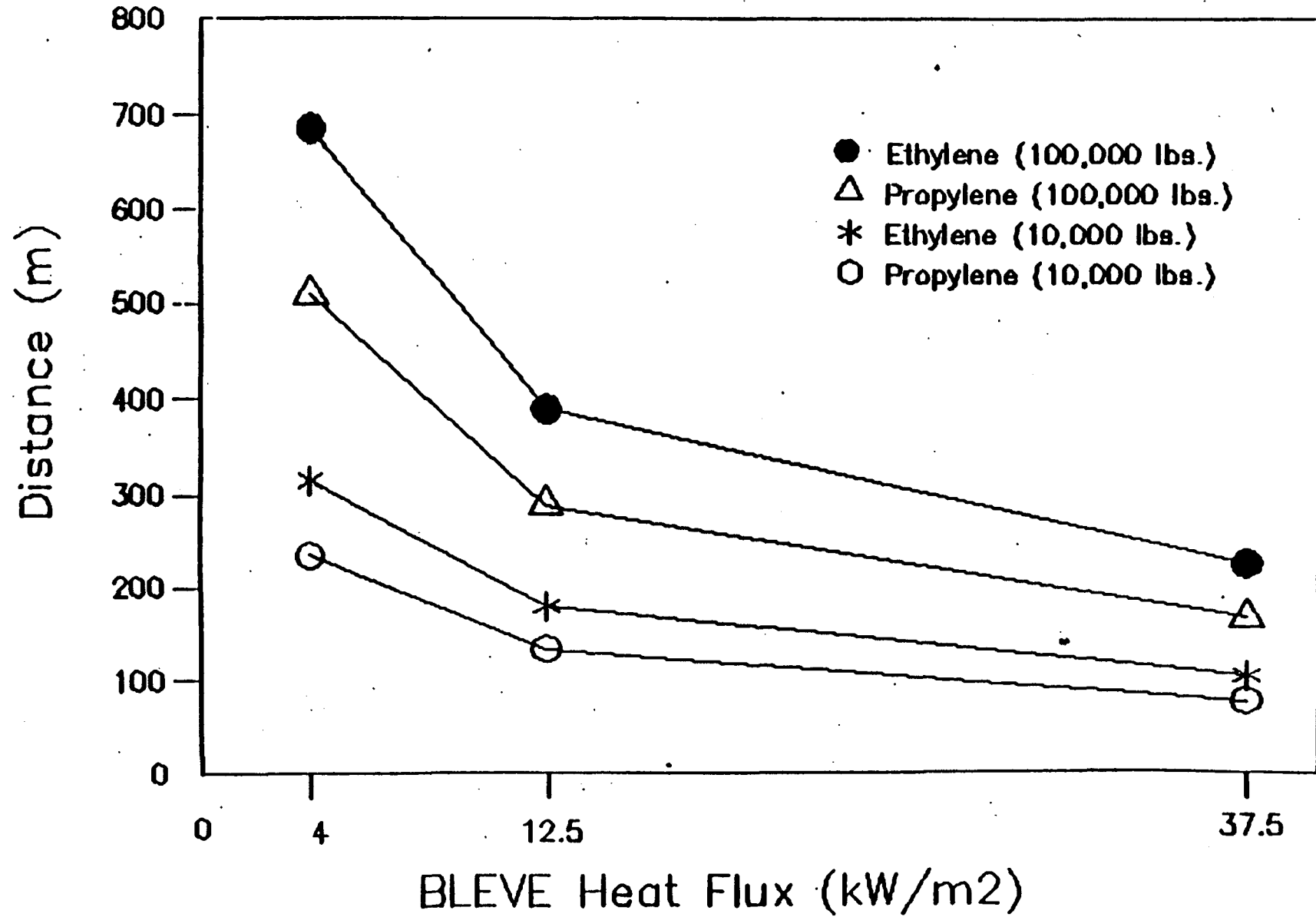
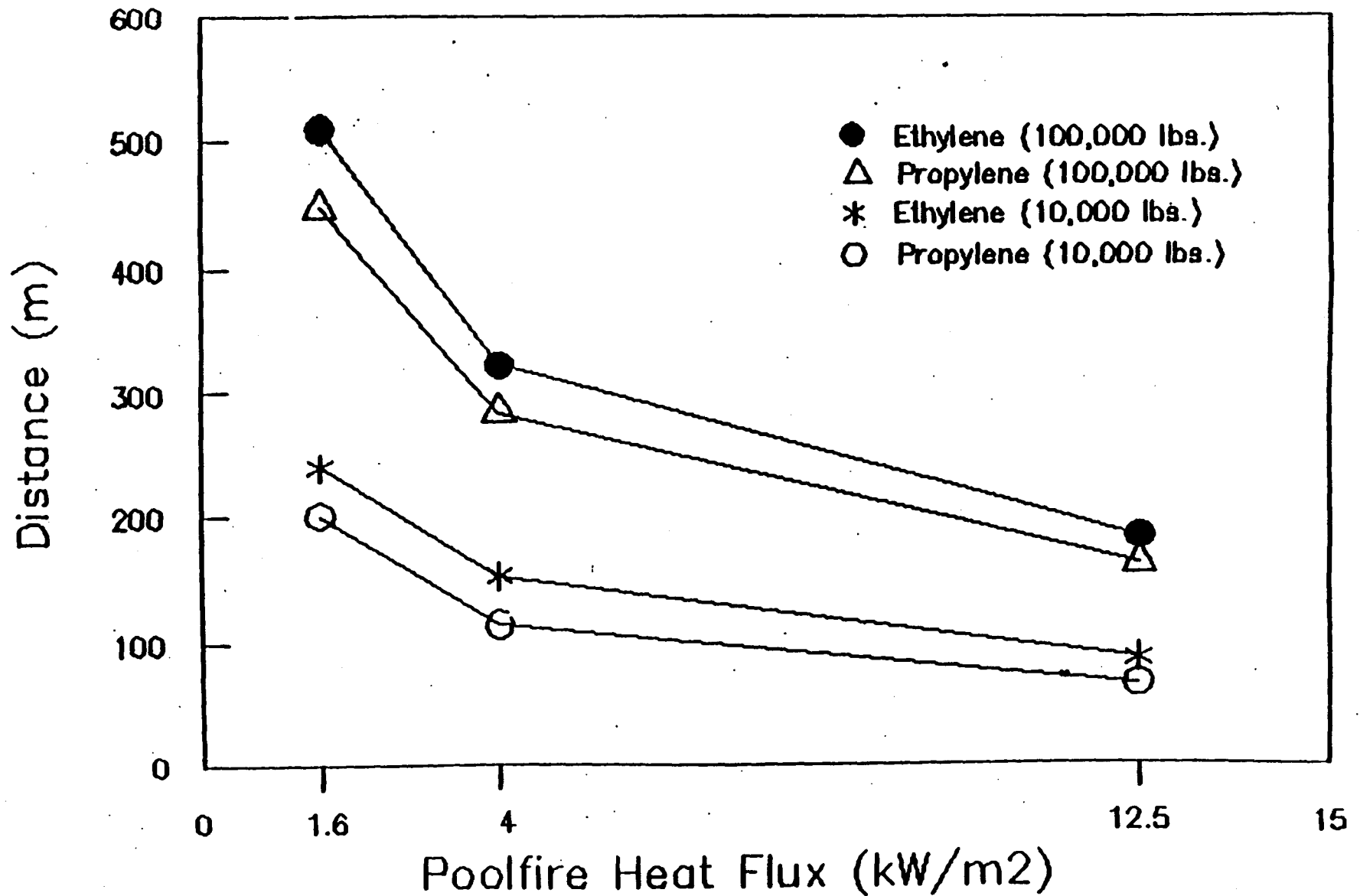


Exhibit C-11  
HAZARD CRITERIA COMPARISON FOR POOL FIRES,  
INSTANTANEOUS RELEASES





#### C.4 References

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## APPENDIX D

### COMPARISON OF RESULTS OF MODELING BY DIFFERENT METHODS AND RESULTS OF VARYING RELEASE SCENARIOS AND METEOROLOGICAL CONDITIONS

#### D.1 Vapor Cloud Explosion Results

Exhibit D-1 presents the results of modeling using several methods for vapor cloud explosions based on 0.5 psi overpressure. This exhibit shows the maximum distance at which the models indicate that the chosen overpressure would be reached. For releases of 100,000 pounds of gases, distances of 326 to 1,165 meters were calculated.

The distances obtained from WHAZAN, the Yellow Book, and ARCHIE at each overpressure level agree quite well with each other, although the WHAZAN and Yellow Book distances for vapor cloud explosions for ethylene and propane are significantly lower than the distances obtained from ARCHIE. These two gases are assumed to be stored at reduced temperatures. The WHAZAN and Yellow Book vapor cloud explosion calculations are based on the quantity of gas immediately flashed into vapor on release, and this quantity depends on the difference between the temperature of the released gas and its boiling point. As ethylene and propane are assumed to be stored at temperatures not far above their boiling points, the fraction calculated to be immediately flashed into vapor (i.e., the quantity that may be involved in a vapor cloud explosion) is relatively small. ARCHIE, on the other hand, assumes that all the material in a container of pressurized gas is released to the air as a gas-aerosol mixture unless the storage temperature is more than 10°C below the boiling point of the gas. For ethylene and propane, the assumed storage temperature, though below ambient temperature, is greater than the boiling point; therefore, ARCHIE, unlike WHAZAN and the Yellow Book, does not yield consequence distances for these two gases that are significantly lower than those for the other gases. If the storage temperature is more than 10°C below the boiling point, ARCHIE assumes the material is released as a liquid, and, therefore, no vapor cloud explosion results are obtained.

ARCHIE produced vapor cloud explosion results for the liquids modeled; however, a disclaimer was provided in the accompanying manual and on the output results pointing out that "incidents involving tanks that are designed to operate at atmospheric pressure are very rare." An additional disclaimer stated that clouds or plumes containing less than 1,000 pounds of vapor or gas are very unlikely to explode when completely unconfined; modeling indicated that for heptane, toluene, and p-xylene, there would be less than 1,000 pounds of vapor released. Because of these disclaimers, the ARCHIE vapor cloud explosion results for the liquids modeled are not included in Exhibit D-1.

#### D.2 Vapor Cloud Fire Results

Exhibit D-1 includes vapor cloud fire results calculated by five methods for releases of 100,000 pounds. The distances given are downwind distances for dispersion to a concentration equal to 50 percent of the LFL. For the Yellow Book, results for gases were calculated based on both the quantity of gas immediately flashed into vapor upon release and on the remaining liquefied gas evaporating from a pool after flashing; note that the distances obtained using the quantity flashed into vapor are significantly larger than those calculated using the evaporating pool, except in the cases of the two gases assumed to be stored at reduced temperatures. For these two gases, ethylene and propane, the distances calculated based on the evaporating pool are greater than the distances based on the quantity flashed. Results from the AIChE course material for gases are based only on the quantity flashed, as recommended. The distances calculated for ethylene and propane, the gases assumed stored at reduced temperatures, are considerably lower than the distances for the two gases assumed stored at ambient temperature. Distances obtained for gases using the Green Book methodology are generally lower than those found by the other methods, probably because the Green Book recommends assuming total release of the gas over a ten minute period, while the other methods assume an instantaneous release. The distances calculated using the Green Book method, which does not take storage temperature into account, are higher than other results only in the cases of the Yellow Book results for the flashed fraction of ethylene and propane (the gases assumed stored at reduced temperatures).

-D-2-

Exhibit D-1

RESULTS OF MODELING BY ALL METHODS

I. WHAZAN Modeling Results for Instantaneous Releases, Moderate and Worst Case Meteorology, and Prolonged Releases, Moderate Meteorology (100,000 pounds)

Chemical	Instantaneous Release Moderate Meteorology Distance (meters)					Instantaneous Release Worst Case Meteorology Distance (meters)				Prolonged Release Moderate Meteorology Distance (meters)			
	Boiling Point (K)	VCE (0.5 psi)	VCF (50%LFL)	BLEVE (12.5 kW/m <sup>2</sup> )	Pool Fire (12.5 kW/m <sup>2</sup> )	VCE (0.5 psi)	VCF (50% LFL)	BLEVE (12.5kW/m <sup>2</sup> )	Pool Fire (12.5 kW/m <sup>2</sup> )	VCF (50%LFL)	BLEVE (12.5kW/m <sup>2</sup> )	Pool Fire (12.5kW/m <sup>2</sup> )	Jet Fire (12.5kW/m <sup>2</sup> )
Ethylene	171	457	1390	388	181	457	6350	388	181	79	388	17	**
Propylene	227	1121	706	287	160	1121	2900	287	160	18	287	15	42
Propane	229	392	747	278	183	392	3100	278	183	73	278	17	**
Butane	275	766	460	269	176	766	1790	269	176	20	269	9	21
Ethylene Oxide	282	443	338	206	109	*	*	*	*	*	*	*	*
Ethyl Chloride	286	268	262	178	97	*	*	*	*	*	*	*	*
Acetaldehyde	293	130	451	200	107	*	*	*	*	*	*	*	*
Pentane	313	**	341	269	182	**	1280	269	182	21	269	23	**
Acetone	329	**	214	**	116	*	*	*	*	*	*	*	*
Gasoline	332	**	338	**	175	**	1270	**	175	64	**	16	**
Hexane	345	**	233	**	174	**	842	**	174	56	**	15	**
Trichloro- ethylene	360	**	52	**	**	*	*	*	*	*	*	*	*
Heptane	375	**	173	**	168	**	604	**	168	57	**	15	**
Toluene	383	**	154	**	153	**	535	**	153	67	**	16	**
Acetic Acid	391	**	98	**	**	*	*	*	*	*	*	*	*
p-Xylene	410	**	110	**	152	**	374	**	152	65	**	16	**
Benzaldehyde	452	**	30	**	109	*	*	*	*	*	*	*	*
Dimethyl Sulfoxide	462	**	41	**	86	*	*	*	*	*	*	*	*

\* Analysis was not carried out

\*\* No results were obtained from analysis, or results were not included, based on evaluation.

VCE = Vapor Cloud Explosion

VCF = Vapor Cloud Fire

**Exhibit D-1 (continued)**  
**RESULTS OF MODELING BY ALL METHODS**

**II. Modeling Results Using Other Methods for Instantaneous Releases, Moderate Meteorology**  
**(100,000 pounds)**

Chemical	ARCHIE Results					Yellow Book Results				AIChE Manual Results			Green Book Results	
	Distance (meters)					Distance (meters)				Distance (meters)			Distance (meters)	
	Boiling Point	VCE	VCF	BLEVE	Pool Fire	VCE	VCF (Gases)	VCF (All)	Pool Fire	VCF (Gases)	VCF (Liquids)	Pool Fire	VCF	
	(K)	(0.5 psi)	(50% LFL)	(10kW/m <sup>2</sup> )	(10kW/m <sup>2</sup> )	(0.5 psi)	Flash Fraction	Pool Evaporation	(12.5 kW/m2)	Flash Fraction	Pool Evaporation	(12.5kW/m2)	(50% LFL)	
							(50% LFL)	(50% LFL)		(50% LFL)	(50% LFL)			
Ethylene	171	867	770	285	**	415	330	922	134	452	**	299	371	
Propylene	227	682	751	285	**	932	862	554	112	1165	**	188	350	
Propane	229	683	733	285	**	326	261	586	137	355	**	225	332	
Butane	275	680	712	285	**	635	547	242	120	720	**	190	310	
Pentane	313	**	453	**	151	**	**	239	120	**	187	221	165	
Gasoline	332	**	447	**	137	**	**	216	107	**	170	213	163	
Hexane	345	**	160	**	151	**	**	115	112	**	95	206	86	+
Heptane	375	**	112	**	153	**	**	60	106	**	53	202	50	+
Toluene	383	**	97	**	150	**	**	42	86	**	38	169	44	+
p-Xylene	410	**	0	**	144	**	**	22	86	**	21	166	28	+

\* Analysis was not carried out.

\*\* No results were obtained from analysis, or results were not included, based on evaluation.

+ Method is not valid for distances less than 100 meters.

VCE = Vapor Cloud Explosion

VCF = Vapor Cloud Fire

Results for chemicals that are liquids at ambient temperatures are based on evaporating pools for all the models (see Appendix B for details). Distances to a concentration equal to 50 percent of the LFL for vapor cloud fires range from 261 to 1,390 meters for gases; distances are generally smaller for liquids, although significant distances result for volatile liquids (e.g., distances calculated by the various methods range from 165 to 453 meters for pentane). Distances obtained using the Green Book dispersion modeling calculations are not valid for less than 100 meters; therefore, the Green Book results for four relatively non-volatile liquids should be disregarded. It is possible that distances less than 100 meters obtained from some of the other methods may also be invalid, as similar methods appear to be used in the calculations.

### D.3 BLEVE Results

Exhibit D-1 presents the results obtained using WHAZAN and ARCHIE to model BLEVEs for 100,000 pound releases. WHAZAN results are shown for a heat radiation level of 12.5 kW/m<sup>2</sup> for WHAZAN. The distance reported as the "fatality distance" on the ARCHIE output results is presented in this exhibit. BLEVEs are not modeled in ARCHIE; however, since fireballs are generally associated with BLEVEs, these results from the ARCHIE model are presented in Exhibit D-1 for comparison to WHAZAN BLEVE results. The other models used for consequence analysis did not include methods for analyzing BLEVEs.

ARCHIE results are based on fireball size and heat radiation (see Appendix C, Section A.1.10). According to the ARCHIE manual, the fatality level corresponds to a heat flux in excess of 160 kilojoules per square meter (kJ/m<sup>2</sup>). Using the fireball duration of 15 seconds to convert the heat radiation level from kJ/m<sup>2</sup> to kW/m<sup>2</sup> indicates that the ARCHIE fatality level is about 11 kW/m<sup>2</sup>, which is very close to 12.5 kW/m<sup>2</sup>, used by WHAZAN. Note, however, that WHAZAN gives a BLEVE duration of 36 seconds while ARCHIE gives a duration of 15 seconds for a 100,000 pound release.

The ARCHIE model gives a fatality distance of 285 meters for all the chemicals modeled; the lack of variation by chemical is probably due to the fact that, according to the ARCHIE manual, ARCHIE assumes that the chemical modeled is propane or has similar characteristics. WHAZAN consequence distances range from 178 meters to 387 meters for a heat radiation level of 12.5 kW/m<sup>2</sup>.

### D.4 Pool Fire Results

Results of modeling using different methods for pool fires, showing the maximum distance at which a heat radiation level of 12.5 kW/m<sup>2</sup> (10 kW/m<sup>2</sup> for ARCHIE) is reached, are presented in Exhibit D-1. The WHAZAN model indicated that the pool fires of the chemicals modeled would last 60 seconds or more; as stated in the WHAZAN manual, it might be possible to "shelter" from the fire within about 30 seconds to one minute.

Differences between chemicals modeled by each method are relatively small. The distances calculated by different methods are in reasonably good agreement with each other. The calculations based on the AIChE-sponsored materials gave the greatest distances (166 to 299 meters), while the Yellow Book method gave the smallest (86 to 134 meters). The ARCHIE model does not give pool fire results for gases. The other models allow the calculation of results for gases; the results for gases differ little from the results for liquids. The distances found for pool fires for 100,000 pound releases of gases for a heat radiation level of 12.5 kW/m<sup>2</sup> are smaller than the distances for vapor cloud explosions for the same quantity modeled at 3.0 psi or lower, except for gases assumed stored at reduced temperatures. Vapor cloud fire results (for 50 percent of the LFL) and BLEVE results (for 12.5 kW/m<sup>2</sup>) for gases are larger than the pool fire results. For relatively volatile liquids (e.g., pentane), vapor cloud fire distances are generally greater than pool fire distances; for less volatile liquids, distances calculated by most of the methods are greater for pool fires.

## **D.5 Jet Fire Results**

Jet fire results, which are, by definition, prolonged releases, were obtained only for propylene and butane, the two gases assumed to be liquefied under pressure. For jet fires, the release was assumed to take place from a 1.5 inch hole in a tank 12 feet in diameter. Results are shown for 100,000 pound releases in Exhibit D-1 for a heat flux level of  $12.5 \text{ kW/m}^2$ . Jet fires of propylene and butane under these conditions gave distances that are smaller than any of the distances for any other accident type resulting from instantaneous releases. Distances for jet fires are somewhat greater, however, than for vapor cloud fires or pool fires resulting from prolonged releases under the same conditions.

## **D.6 Instantaneous Release Compared to Prolonged Release**

Ten hydrocarbons studied were modeled using the prolonged release scenario in the WHAZAN linked model for comparison with the modeling results for instantaneous release. The WHAZAN linked model (prolonged release) was run for 100,000 pounds of each chemical assuming the same meteorological conditions (3.0 meters per second wind speed and D wind stability), and storage conditions as for the instantaneous release. To simulate a prolonged release, a 1.5 inch hole in a 12 foot diameter tank was assumed. The average evaporation rate for the pool, as determined in the linked model, was then used to run the WHAZAN stand-alone model for buoyant plume dispersion (see Appendix B.1 for more information).

Exhibit D-1 shows results of WHAZAN modeling for prolonged releases of ten chemicals, where release was assumed to take place from 1.5 inch diameter holes in 12 foot diameter tanks. Distances to 50 percent of the LFL for vapor cloud fires are much smaller (18 to 79 meters) than for instantaneous releases.

For pool fires, prolonged releases also result in much smaller consequence distances than instantaneous releases. As was the case for instantaneous releases, the consequence distance varies little from chemical to chemical. The magnitude of the results curve is much smaller for prolonged releases than for instantaneous releases, and all of the prolonged release consequence distances are less than 25 meters.

WHAZAN did not produce vapor cloud explosion results for prolonged releases. As shown in Exhibit D-1, WHAZAN produced BLEVE results for prolonged releases that are identical to the results for instantaneous releases. It is not clear what these results mean, since BLEVEs seem to be instantaneous releases by definition (see Section 6.3).

## **D.7 Moderate Meteorology Compared to Worst Case Meteorology**

Ten hydrocarbons were modeled using WHAZAN to determine the effect on consequence distances of using worst case meteorology rather than moderate meteorology. The WHAZAN linked model (instantaneous release) was run for 100,000 pounds of each chemical using the same storage temperatures and pressures as used with moderate meteorology. Worst case meteorological conditions (1.5 meters per second wind speed and F wind stability) were used rather than moderate meteorological conditions (3.0 meters per second wind speed and D wind stability). The average evaporation rate for the pool, as determined in the linked model, was used to run the WHAZAN stand-alone model for buoyant plume dispersion. Various other default values were used in the model; these values are summarized in Appendix E.

Exhibit D-1 includes vapor cloud fire results from WHAZAN for ten chemicals using worst case meteorological conditions of wind speed of 1.5 meters per second and F atmospheric stability. The WHAZAN results appear to be strongly dependent on the meteorological assumptions made, with distances determined using worst case meteorology being much greater than those resulting from modeling using moderate meteorology. As shown in Exhibit D-1, distances under worst case meteorological conditions extend from 1,790 to 6,350 meters for gases, compared to 460 to 1,390 meters under moderate conditions. For the other consequence types, the results were the same for both meteorological conditions, indicating that varying meteorological conditions probably have little effect on the potential consequences of vapor cloud explosions, BLEVEs, and pool fires.



## APPENDIX E

### INPUTS FOR MODELING

This appendix presents the inputs for the consequence analyses. Temperatures and pressures assumed as storage conditions for each of the chemicals modeled are listed in Exhibit E-1. Exhibit E-2 presents the physical/chemical property data used for modeling. The data shown were used for WHAZAN modeling, which required more data than the other methods. The same data were used as required for modeling by the other methods; in some cases the methods required conversion of the data to different units. Exhibit E-3 shows the assumptions used for WHAZAN modeling for instantaneous releases and moderate meteorology. The same meteorological assumptions were used in modeling by the other methods. Assumptions for WHAZAN modeling of prolonged releases are shown in Exhibit E-4, and assumptions for WHAZAN modeling under worst-case meteorological conditions are shown in Exhibit E-5. Modeling for prolonged releases and for worst-case meteorology was done only with WHAZAN. Exhibit E-6 presents the data and assumptions used for ARCHIE modeling.

Exhibit E-1  
Temperatures and Pressures Used in Scenarios

Chemical	Storage Conditions	
	Temp.(°K)	Press.(Bars)
<u>Gases</u>		
Ethylene	175	1.3
Propylene	293	13.3
Propane	232	1.3
Butane	293	6.3
Ethylene oxide	293	6.18
Ethyl chloride	288	1.3
<u>Liquids</u>		
Acetaldehyde	293	1.013
Pentane	293	2.74
Gasoline	293	1.013
Hexane	293	1.013
Heptane	293	1.013
Toluene	293	1.013
p-Xylene	293	1.013
Acetone	293	1.013
Trichloroethylene	293	1.013
Acetic acid	293	1.013
Benzaldehyde	293	1.013
Dimethyl sulfoxide	293	1.013

-E-3-  
Exhibit E-2  
Chemical Data Used for Models  
A. Hydrocarbons

PROPERTIES	Ethylene	Propylene	Propane	Butane	Pentane	Gasoline	Hexane	Heptane	Toluene	p-Xylene
CAS Number	74851	115071	74986	75285	109660	8006619	110543	142825	108883	106423
Liquid Heat Capacity (J/kg/K)	2750.0	2500.0	2400.0	2500.0	2207.0	2056.0	2456.19	2605.74	1738.0	1750.0
Liquid Density (kg/cube m)	569.0	520.0	590.0	600.0	626.0	732.0	659.0	683.8	867.0	861.0
Gamma Ratio of Specific Heat	1.255	1.152	1.13	1.092	1.086	1.054	1.063	1.045	1.089	1.071
Heat of Evaporation (J/kg)	4.83e+05	4.38e+05	4.26e+05	3.90e+05	3.67e+05	3.20e+05	3.35e+05	3.17e+05	3.61e+05	3.40e+05
Heat of Combustion (J/kg)	-4.72e+07	-4.58e+07	-4.60e+07	-4.54e+07	-4.54e+07	-4.35e+07	-4.48e+07	-4.46e+07	-4.06e+07	-4.08e+07
Lower Flammability Limit (fract.)	0.027	0.020	0.021	0.018	0.015	0.014	0.014	0.012	0.012	0.011
Upper Flammability Limit (fract.)	0.286	0.111	0.095	0.084	0.078	0.074	0.074	0.067	0.070	0.070
Boiling Point at 1 Atmos. (K)	170.828	227.423	229.273	274.843	312.669	332.226	344.589	374.557	383.111	410.05
Molecular Weight	28.05	42.08	44.09	58.12	72.15	72.00	86.17	100.21	92.00	106.00
Vapor Heat Capacity (J/kg/K)	700.0	1000.0	1100.0	1200.0	1547.0	1234.0	1819.0	1992.26	1122.0	1193.0
Critical Temperature (K)	283.1	365.0	369.8	425.0	469.7	787.0	507.4	540.7	592.0	616.2
Saturated Vapor Pressure (Bara)	--	11.717	9.622	2.282	0.593	0.501	0.175	0.055	0.039	0.012
Liquid Enthalpy (J/kg)	-6.69e+05	-4.35e+05	-4.33e+05	-4.37e+05	-4.33e+05	0.00	-4.25e+05	-4.23e+05	3.17e+05	0.00
Vapor Enthalpy (J/kg)	-396000	-65000	-62000	-81000	-40400	390000	-40200	-40200	746000	417000
Vapor Entropy (J/kg/K)	-131.1	-131.7	-144.2	-54.4	-157.0	-1429.0	-171.6	-203.3	-2732.6	-1527.5
Saturated Vapor Temperature (K)	171.049	227.71	229.575	275.183	313.056	332.952	344.995	374.993	383.553	410.509
Vapor Density (kg/cube m)	1.163	1.744	1.828	2.409	--	--	--	--	--	--

-E-4-  
Exhibit E-2  
Chemical Data Used for Models  
B. Non-Hydrocarbons

PROPERTIES	Acetaldehyde	Acetone	Dimethyl Sulfoxide	Trichloro-Ethylene	Ethyl Chloride	Ethylene Oxide	Acetic Acid	Benzaldehyde
CAS Number	75070	67641	67685	79016	75003	75218	64197	100527
Liquid Heat Capacity (J/kg/K)	2483.09	2176.0	1957.63	946.58	1616.98	1979.0	2048.2	1676.3
Liquid Density (kg/cube m)	783.4	789.9	1095.4	1464.2	897.8	869.0	1042.9	1041.5
Gamma Ratio of Specific Heat	1.182	1.127	--	1.116	1.155	1.212	1.145	1.10
Heat of Evaporation (J/kg)	5.69e+05	5.11e+05	6.03e+05	2.40e+04	3.79e+05	5.80e+05	4.05e+05	3.62e+05
Heat of Combustion (J/kg)	-2.51e+07	-2.86e+07	-1.98e+07	-6.58e+06	-1.99e+07	-2.67e+07	-1.31e+07	-3.20e+07
Lower Flammability Limit (fract.)	0.016	0.026	0.026	0.125	0.038	0.03	0.054	0.015
Upper Flammability Limit (fract.)	0.104	0.128	0.285	0.90	0.154	1.00	0.16	0.10
Boiling Point at 1 Atmos. (K)	293.55	329.44	462.15	360.1	285.42	281.814	391.05	452.2
Molecular Weight	44.053	58.08	78.129	131.389	64.514	44.05	60.052	106.124
Vapor Heat Capacity (J/kg/K)	946.63	1296.7	459.88	390.38	970.9	1006.0	1114.0	981.8
Critical Temperature (K)	461.0	0.306	726.0	571.0	460.35	469.0	592.71	694.8
Saturated Vapor Pressure (Bara)	1.198	513671	0.000812	0.0983	1.588	1.699	0.016	0.0009
Liquid Enthalpy (J/kg)	7.40e+05	2.84e+05	5.84e+05	2.82e+05	3.42e+05	-6.29e+05	4.72e+05	5.00e+05
Vapor Enthalpy (J/kg)	282237	5085.23	137113	116392	205523	-26400	226460	292724
Vapor Entropy (J/kg/K)	5679.52	298.15	3920.06	2474.73	4274.73	-100.8	4197.53	--
Saturated Vapor Temperature (K)	298.15	--	298.15	298.15	298.15	282.118	294.30	297.00
Vapor Density (kg/cube m)	--	--	--	--	2.87	1.826	--	--

### A. Hydrocarbons

[illegible]

Exhibit E-3

WHAZAN Modeling Data for Instantaneous Releases, Moderate Meteorology  
B. Non-Hydrocarbons

Data Inputs	Ethylene Oxide	Ethyl Chloride	Acetaldehyde	Acetone	Trichloro ethylene	Acetic Acid	Benzaldehyde	Dimethyl Sulfoxide
Storage Temperature (K)	293.0	288.0	293.0	293.0	293.0	293.0	293.0	293.0
Storage Pressure (Bar)	6.18	1.3	1.013	1.013	1.013	1.013	1.013	1.013
Ambient Temperature (K)	293.0	293.0	293.0	293.0	293.0	293.0	293.0	293.0
Stored Mass (kg)	45360	45360	45360	45360	45360	45360	45360	45360
Bund Area (m2)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Wind Speed (m/s)	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
Max Time of Interest (s)	100000	100000	100000	100000	100000	100000	100000	100000
<b>BUOYANT PLUME DISPERSION</b>								
Effective Release Height (m)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Release Rate (kg/s)	109.6	137.4	102.5	44.51	44.52	30.84	1.38	3.357
Min. Conc. of Interest (ppm)	15000	19000	8000	13000	62500	27000	7500	13000
Wind Speed (m/s)	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
Ambient Temperature (K)	293.0	293.0	293.0	293.0	293.0	293.0	293.0	293.0
Surface Roughness Parameter	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100
Atmospheric Stability Category	D	D	D	D	D	D	D	D

### WILAZAN Modeling Data for Prolonged Releases

[illegible]

### WHAZAN Modeling Data for Instantaneous Releases, Worst Case Meteorology

[illegible]



-E-9-  
Exhibit E-6  
**ARCHIE Modeling Data**

[illegible]

## APPENDIX F

## ADDITIONAL INFORMATION FROM ACCIDENT DATABASES

**F.1 Additional Information from the Acute Hazardous Events Data Base**

The Acute Hazardous Events Data Base (AHE/DB) includes information on 773 incidents for which one of the end effects (up to four end effects may be listed) was fire or explosion. Most of the explosion incidents involved flammable chemicals rather than explosives and, therefore, were included in this analysis of flammable chemical accidents. The first (or primary) end effect was listed as fire or explosion in 542 (70 percent) of such incidents; for most of the others, spill or vapor release was listed as the first end effect, and fire or explosion was second. Of the 773 fire or explosion incidents, 652 (84 percent) took place at a fixed location, while 121 (16 percent) occurred during transportation.

A total of 431 deaths was reported resulting from 88 of the fire or explosion incidents, and 4,195 injuries were reported from 286 incidents. Fire and explosion incidents account for about 13 percent of the total incidents in the AHE/DB, but they account for nearly 92 percent of the deaths and about 36 percent of the injuries reported. Exhibit F-1 graphically presents fire and explosion events and deaths and injuries in fire and explosion events compared to the total in the AHE/DB.

Specific flammable chemicals that the AHE/DB reports as having been involved in two or more in-plant fire or explosion incidents are presented in Exhibit F-2. Number of incidents versus boiling point (as an indication of volatility) is shown; the DOT hazard class and packing group that would be assigned based on flash point and boiling point is also indicated for each chemical (see key). In the case of some fuel chemicals (gasoline, propane, butane, natural gas/methane) the number of in-plant incidents was estimated from the number reported in the 1985 version of the AHE/DB, as fuels have been deleted from the 1988 version, by assuming that the number of incidents would have increased by a factor of 2. The total number of incidents in the 1988 version of the data base was approximately double the number in the 1985 version; therefore, it was assumed that the number of fuel incidents probably also would have approximately doubled.

As Exhibit F-2 shows, a number of flammable gases were reported involved in in-plant fires or explosions, as were several liquids in DOT Packing Group I/NFPA Flammability Rating 4 (i.e., the most flammable and volatile categories). There were also a number of flammable chemicals that fall into DOT packing groups II and III and several chemicals that are considered merely combustible rather than flammable by DOT and NFPA standards. There does not appear to be any clear correlation between physical/chemical properties (flash point and boiling point) and the number of fire and explosion incidents reported for chemicals in the AHE/DB. The severity of the incidents, as indicated by the number of deaths and injuries that resulted, was also considered in relation to the flash points and boiling points of the chemicals. There did not appear to be a clear correlation between the properties of the chemicals and the severity of the incidents. Accidents and resulting consequences are dependent not only upon the physical/chemical properties of the chemicals involved, but also on factors such as location, time, weather, amount, other chemicals nearby, and release conditions; little information on these factors is provided in the AHE/DB.

Production volume for the flammable and combustible chemicals shown in Exhibit F-2 was considered as a possible factor related to the number of incidents reported. Although several high-volume chemicals were involved in relatively large numbers of in-plant incidents (toluene in 17 incidents, gasoline in an estimated 13 incidents, vinyl chloride in 7 incidents), there appears to be no clear correlation between number of incidents and production volume.

In addition to the specific chemicals shown in Exhibit F-2, there were many unknown chemicals and non-specific materials involved in incidents reported in the AHE/DB. A large number of incidents (61) involved unknown substances. Chemical types or categories listed include the following:

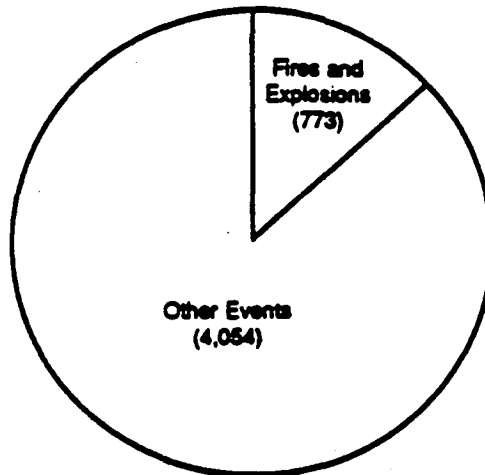
- Alcohol: 3
- Explosives: 14
- Fertilizer: 4
- Flammable chemicals, gas, liquid, or material: 7
- Hazardous waste or industrial waste: 12
- Paint: 7
- Pesticide: 29
- Petroleum products or petroleum refining slurry: 6
- Plastics: 7
- Rubber, rubber hose or tires: 8
- Solvents: 13

Various other non-specific listings also are included, such as several kinds of oil and fuel, and non-chemical materials such as insulated wire.

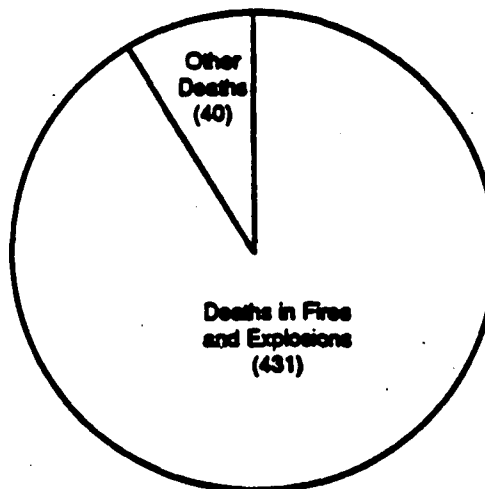
A number of chemicals reported to have been involved in fires or explosions are not flammable or are only slightly flammable (e.g., chlorine (23 incidents), ammonia (19 incidents), hydrochloric acid (12 incidents), nitric acid (11 incidents)). These chemicals were not included in Exhibit 2; their involvement in fires and explosions may be related to their reactivities and other chemicals involved in the incidents rather than to flammability.

**EXHIBIT F-1**  
**FIRE AND EXPLOSION EVENTS COMPARED TO ALL**  
**EVENTS IN ACUTE HAZARDOUS EVENTS DATA BASE**

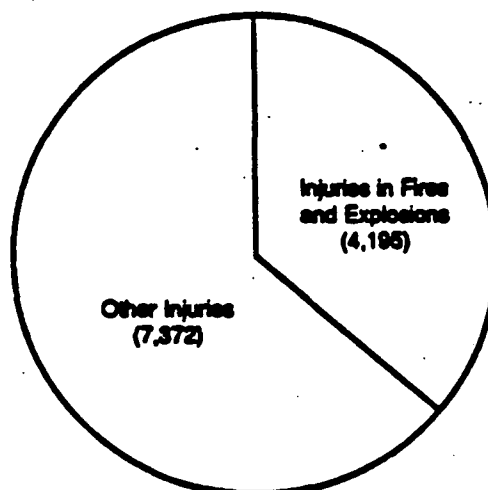
**Fire and Explosion Events Compared to Total Events**



**Deaths in Fire and Explosion Events Compared to Total Deaths**



**Injuries in Fire and Explosion Events Compared to Total Injuries**



### Number of Fire/Explosion Incidents



## KEY FOR EXHIBIT F-2

- Flammable gases (Boiling point  $\leq 20^{\circ}\text{C}$ )  
DOT Hazard Class 2.1 (2.3 for flammable and poison)  
NFPA Flammability Rating 4
- + Flammable liquids, DOT Packing Group I or equivalent  
DOT Hazard Class 3, Packing Group I: Boiling point  $\leq 35^{\circ}\text{C}$   
NFPA Flammability Rating 4: Boiling point  $< 38^{\circ}\text{C}$ , Flash point  $< 23^{\circ}\text{C}$
- ◇ Flammable liquids, DOT Packing Group II or equivalent  
DOT Hazard Class 3, Packing Group II: Boiling point  $> 35^{\circ}\text{C}$ , Flash point  $< 23^{\circ}\text{C}$   
NFPA Flammability Rating 3: Boiling point  $\geq 38^{\circ}\text{C}$ , Flash point  $< 23^{\circ}\text{C}$ ,  
or Flash point  $< 38^{\circ}\text{C}$  and Flash point  $\geq 23^{\circ}\text{C}$
- △ Flammable liquids, DOT Packing Group III or equivalent  
DOT Hazard Class 3, Packing Group III: Boiling point  $> 35^{\circ}\text{C}$ , Flash point  $\geq 23^{\circ}\text{C}$ ,  
Flash point  $< 60.5^{\circ}\text{C}$   
NFPA Flammability Rating 2: Flash point  $> 38^{\circ}\text{C}$ , Flash point  $\leq 93^{\circ}\text{C}$
- X Combustible liquids  
No applicable DOT Hazard Class  
NFPA Flammability Rating 2 or 1 (NFPA 1: Flash point  $> 93^{\circ}\text{C}$ )

## F.2 Additional Information from the ARIP, OSHA, M & M Accident Databases

This section provides additional accident information from the ARIP, OSHA, and M & M Databases.

Exhibit F-3 presents the flammable chemicals most frequently involved in fires and explosions. In the ARIP and OSHA databases, the top five chemicals were listed. For the M & M database, the top 10 chemicals were listed. The data indicate that simple hydrocarbon chemicals are most often involved in fires or explosions. Specifically, the hydrocarbon chemicals most frequently listed are propane, propylene, butane, and methane. Ethylene oxide also was involved in a number of incidents.

**EXHIBIT F-3**  
**FLAMMABLE CHEMICALS INVOLVED IN FIRES AND EXPLOSIONS**

Chemical	Incidents in ARIP database	Incidents in OSHA database	Incidents in M&M database	Total Incidents
Acetylene		2		2
Butane		2	4	6
Cumene			2	2
Ethylene			2	2
Ethylene Oxide	3		3	6
Hydrogen			3	3
Methane/Natural Gas		5		5
Methyl Chloride	1			1
Propane		8	15	23
Propylene	1		6	7
Propylene Oxide			2	2
Silane	1			1
Styrene			2	2
Unspecified flammable gas or liquid		9		9
Unspecified hydrocarbon			4	4

Exhibit F-4 lists the ARIP accidents involving flammable chemicals. Although ARIP collects data on deaths and injuries to the public, none of the flammable chemical fires or explosions involved public health impact. The ARIP accidents indicate that equipment failure is a prevalent cause of flammable chemical explosions.

**EXHIBIT F-4**  
**SUMMARY OF EXPLOSION ACCIDENTS INVOLVING FLAMMABLE CHEMICALS IN THE ARIP DATABASE**

Chemical(s)	Quantity Released in Pounds	Cause/Description	End Effects	Facility		Public		Number Evacuated
				Injuries	Deaths	Injuries	Deaths	
Ethylene Oxide	-	Failure of pump seal due to freezing led to vapor release of ethylene oxide; heat of friction caused fire	Vapor release, fire	0	0	0	0	0
Ethylene Oxide	10	Combination of extreme cold temperatures and hot operating temperatures led to warping and rupture of flange joints, resulting in vapor release of ethylene oxide and subsequent fire	Vapor release, fire	0	0	0	0	0
Ethylene Oxide	12	Valve failure on process vessel allowed atmosphere above ethylene oxide liquid to exceed lower explosion limit, resulting in vapor release, fire and explosion	Vapor release, fire, explosion	0	0	0	0	0
Methyl Chloride	37,502	Explosion occurred during trial operation of new process equipment while reactants were being removed. Explosion damaged process vessels and piping, releasing methyl chloride gases	Explosion, fire, vapor release	1	0	0	0	0



Chemical(s)	Quantity Released in Pounds	Cause/Description	End Effects	Facility		Public		Number Evacuated
				Injuries	Deaths	Injuries	Deaths	
Propylene and Propane	1,000	Operator error during maintenance activity allowed valve to leak propylene and propane vapor and liquid, which ignited leading to subsequent fire and explosions	Vapor release, explosion, fire	2	0	0	0	150
Silane	-	Employees attempted to vent a cylinder of compressed silane gas contaminated with nitrous oxide when it exploded; led to subsequent explosions and fire destroying the entire facility	Explosion, fire	0	2	0	0	0

Exhibit F-5 provides information about explosions in the OSHA data base. The OSHA data tends to cover releases that have on-site rather than off-site consequences. In 1990, 25 employee deaths and 43 injuries were reported for flammable chemical explosions. The causes of these accidents are mostly equipment failure including general pipeline failure, valve failure, process unit failure, and leaking torches. In addition to equipment failure, employee error or misjudgement of hazardous situations frequently contribute to an accident. Operators use equipment that is inappropriate or do not follow standard operating procedures. Also, mistakes by maintenance personnel often cause explosions. In many accidents, inadequate purging of vapors from tanks, wells, or vaults have caused explosions with common ignitions sources including welding torches, gas heaters, pilot lights, lighters, and cigarettes.

**Exhibit F-5**  
**INFORMATION ABOUT EXPLOSION ACCIDENTS INVOLVING FLAMMABLE CHEMICALS**  
**IN THE OSHA DATABASE**

Chemical	Human Factor	Cause	Number of Injuries	Number of Deaths
acetylene	insufficient or lack of engineering controls	generator lost power and acetylene gas accumulated and ignited from a spark from electric control room	1	0
acetylene	misjudgment of hazardous situation	employee filled bag with acetylene to ignite as practical joke; static spark ignited bag prematurely	2	0
aluminum dust	malfunction in securing/warning operation	welding sparks ignited dust and aluminum fines creating fire ball	7	0
butane	misjudgment of hazardous situation	butane leak ignited	1	1
butane	butane lighter carried in clothing	hot slag ignited butane lighter	0	1
2-butanone	misjudgment of hazardous situation	employee purging spray paint gun on top of drum left generator operating; voltage from generator passed through metal plumbing and ignited drum	2	1
carbon monoxide	insufficient or lack of engineering controls	gas heater ignited CO and other flue gases	0	1
flammable liquid containing toluene and naphtha	insufficient/lack of practice procedures	piece of slag or spark from welding ignited vapors	0	1
flammable liquid	misjudgment of hazardous situation	gas cutting torch ignited tank previously containing flammable liquid	1	0
flammable liquid	equipment inappropriate for operation	gas space heater ignited spilled flammable liquid	0	1
flammable liquid	misjudgment of hazardous situation	cigarette lighter ignited clothing splashed with flammable liquid	2	1
flammable liquids	misjudgment of hazardous situation	electric arc welder ignited waste oil tank with oil and flammable liquids	1	1
flammable vapor cloud	unknown	a released vapor cloud ignited and exploded	3	2

Chemical	Human Factor	Cause	Number of Injuries	Number of Deaths
flammable vapors	used unapproved equipment in flammable atmosphere/misjudgment of hazardous situation	electric skill saws ignited vapors in tank	1	1
flammable vapors	equipment inappropriate for operation	static electricity ignited vented vapors which caused a vessel explosion	0	1
flammable vapors	equipment inappropriate for operation	gas-powered water heater ignited vapors in spray paint booth	1	0
flammable vapors	misjudgment of hazardous situation	employee scraping underground storage tank ignited vapors with oxygen-acetylene torch	0	1
hydrogen	misjudgment of hazardous situation	chemical reaction occurred within tank producing hydrogen gas; ignited gas with torch when opening tank	1	2
liquified propane gas	malfunction in securing/warning operation	gas leak caught on fire	0	1
liquified propane gas	disconnected gas line	match ignited liquified propane gas from disconnected line	1	0
methane	misjudgment of hazardous situation	cigarette lighter ignited natural gas vapors from damaged utility line	3	0
methane	malfunction in securing/warning operation	open check valve allowed hydrocarbon gas to escape and ignite	8	1
molten aluminum	malfunction in securing/warning operation	aluminum billet mold fell into coolant and molten aluminum exploded	1	0
natural gas	misjudgment of hazardous situation	spark from engine ignited gases from oil and natural gas well	1	4
natural gas	insufficient or lack of practice procedures	leaking cutting torch ignited electrode holder causing explosion	0	1
natural gas	misjudgment of hazardous situation	dozer blade ignited gas line	0	1
propane	malfunction in securing/warning operation	unrepaired gas leak in smokehouse pilot light caused fire in smokehouse burner	1	0
propane	insufficient or lack of practice procedures	match struck inside underground utility vault ignited propane gas	1	1

Chemical	Human Factor	Cause	Number of Injuries	Number of Deaths
propane	misjudgment of hazardous situation	cigarette ignited propane leaking from tank	1	0
propane	misjudgment of hazardous situation	torch flamed out allowing unburned propane to accumulate and explode	0	1
propane	safety devices removed/inoperable	gas pocket formed and exploded when pilot on grill was lit	1	0
propane	malfunction in securing/warning operation	pilot light ignited gas escaping from seemingly closed tank valve	2	0

Exhibit F-6 covers flammable chemical accidents in the M & M data base. M & M lists dollar damage estimates as well as most off-site damage. Off-site damage occurs less frequently than on-site damage and is more difficult to characterize and measure. Most damage is measured in terms of windows broken. Flying shards of glass would cause injuries and possible death to nearby public residents. In the most forceful explosions, windows were broken 9.6 kilometers (six miles) away from the explosion center. From the M & M data, it appears that simple hydrocarbon chemicals are responsible for many of the explosions causing off-site damage. The reason may be that these chemicals are produced in large quantities and when released, form detonable vapor clouds.

**EXHIBIT F-6**  
**INFORMATION ABOUT EXPLOSION ACCIDENTS INVOLVING FLAMMABLE CHEMICALS IN THE M & M DATABASE**

Chemical	Incident	Type of Facility	Cause/Description	Damage	Consequences		Other Factors About Explosion
					On-site	Off-site	
Butane	Billings, MT (8/14/72)	Refinery	Valve on deisobutanizer blocked by powder. When flange was opened, powder blew out, releasing the liquid butane.	\$14 million	Drums destroyed, fractionation tower fell across two major pipelines.		•Vapors ignited at furnace 100 feet from point of release.
Butane	Pampa, TX (11/14/87)	Petrochemical Plant	Explosion in either an air pipeline or a manifold at an acetic acid production reactor led to release of gas from ruptured pipe, resulting in vapor cloud which exploded	\$241.1M	Destruction of most buildings and heavy damage to most process units	Rupture of an underground fire main	•Reactor maintained at 285° and 700 psi •Ignition occurred 10 seconds after release
Butane (liquid)	Feyzin (Lyon), France (1/4/66)	Refinery	Improper sampling procedures.	\$69 million	Five tanks destroyed, 40 lines cut.		•Ignition 300 feet from point of release •Projectiles up to 100 tons travelled 3/4 of a mile •Ignition occurred 35 minutes after release
Cumene	Deer Park, TX (5/17/80)	Petrochemical Plant	Seal on pump failed.	\$26 million	Fin-fan coolers collapsed; one process column destroyed.		
Cumene	Philadelphia, PA (3/9/82)	Petrochemical Plant	Upset temperature condition caused cumene to be vented.	\$29 million	Three process tanks and one fuel oil tank were destroyed.		
Cyclohexane	Flixborough, UK (6/1/74)		Failure of pipeline on bellows unit.		Firestorm followed vapor cloud explosion.		•60,000 pounds released at 155°C •Vapor cloud 500 ft x 400 ft
Ethane and Propane	Baton Rouge (12/24/89)	Refinery	Ruptured pipe due to cold weather led to vapor cloud release, which ignited resulting in vapor cloud explosion	\$44.7M	Fire damage to 2 large storage tanks, 12 small tanks; ruptured pipelines facility shutdown for 3 days	Damage to windows 6 miles away; damage to electric, steam, and fire water supplies	•Pipeline ruptured at 700 psi •Ignited a few minutes after release •3.6 million gallons of diesel fuel and 880,000 gallons of lube oil were ignited
Ethylene	Pasadena, TX (10/23/89)	Petrochemical Plant	Release of gas (cause unknown) at high pressure led to formation of a large vapor cloud which ignited, resulting in a major initial explosion and later multiple explosions	\$500 to \$750M	Destruction of 2 major process units; stoppage of production for 18 to 24 months		•Ethylene released at 700 psi •Ignition occurred one minute after release •TNT equivalent of 10 tons

Chemical	Incident	Type of Facility	Cause/Description	Damage	Consequences		Other Factors About Explosion
					On-site	Off-site	
Ethylene Oxide	Doe, KY (4/17/62)		Unexpected reaction in storage tank due to ammonia contamination.				<ul style="list-style-type: none"> <li>•45,000 pounds released</li> <li>•TNT equivalent of 16 tons</li> </ul>
Ethylene Oxide	Port Lavaca, TX March 12, 1991	Petrochemical Complex (Ethylene Oxide Plant)	Explosion and fire occurred in an ethylene oxide unit.	\$50 to \$75 million	Destroyed refining column in ethylene oxide plant. Electrical power was lost.	• 6 people driving outside the plant were injured.	<ul style="list-style-type: none"> <li>•Blast was heard 10 miles away</li> <li>•25 area residents were evacuated</li> </ul>
Ethylene Oxide, Propylene Oxide, Glycol and Glycerin	Geismar, LA (5/24/76)	Petrochemical Plant	Process upset.	\$17 million	Tank ruptured.		<ul style="list-style-type: none"> <li>•Projectile (reactor head) thrown 1400 feet</li> </ul>
Ethylene, Propylene	Priola, Italy (5/19/85)	Petrochemical Plant	Flange leak in either boiler or in relief system piping.	\$73 million	Five of eight tanks collapsed or exploded; pipe racks and water control centers were severely damaged.		<ul style="list-style-type: none"> <li>•Propylene released at 375 psi</li> <li>•Projectile skyrocketed 1500 feet in the air</li> </ul>
Flammable solvent	Cincinnati, OH July 19 1990	Resin can-coatings plant	Overpressurization in a reactor vessel discharged flammable liquids and vapors which were ignited by a spark.	\$1.06 million on OSHA settlement	Much of the plant was destroyed. 162 buildings were damaged.	<ul style="list-style-type: none"> <li>•Windows were broken up to .25 miles away.</li> <li>•Nearby homes were damaged in the blast.</li> </ul>	Causes include: <ul style="list-style-type: none"> <li>•Lack of written procedures for solvent cleaning of reactors</li> <li>•Failure to train employees about chemical hazards</li> <li>•Improperly labeled hazardous chemical tanks and containers</li> </ul>
Gas	Abqaiq, Saudi Arabia (4/15/78)	Gas Processing Plant	Internal corrosion of gas transmission pipeline.	\$91 million			<ul style="list-style-type: none"> <li>•Seven minutes between failure and release</li> <li>•Release ignited 1,500 feet from source</li> <li>•Overpressures of 7.8 psi</li> <li>•Projectile thrown 400 feet</li> </ul>
Gas (Fuel)	Abqaiq, Saudi Arabia (6/4/77)	Gas Processing Plant	Gas line failed.	\$19 million			<ul style="list-style-type: none"> <li>•Vapor cloud size was 300 feet x 600 feet</li> <li>•Gas line operating at 500 psi</li> </ul>
Hydrocarbon liquid and gases	Beaumont, TX (11/29/74)	Petrochemical Plant	Discharge caused by broken expansion joint in the section line of a pump.	\$37 million	Process lines broke, causing multiple fires. A second, more serious explosion, destroyed a storage tank.		<ul style="list-style-type: none"> <li>•16,800 gallons of in-process hydrocarbon liquids and gases were released</li> <li>•20,000 gallon storage tank holding isoprene ruptured</li> </ul>



Chemical	Incident	Type of Facility	Cause/Description	Damage	Consequences		Other Factors About Explosion
					On-site	Off-site	
Hydrocarbons	Pernis, Netherlands (1/20/68)	Refinery	Runaway reaction in slop tank resulted in boil over and vapor release.	\$98 million	Two wax cracking units, one naphtha cracking unit, one sulfur plant, and 80 storage tanks were either destroyed or damaged.	• Damages reported up to 9 1/2 miles away	<ul style="list-style-type: none"> <li>• Between 50 and 100 tons of hydrocarbon slop boiled over</li> <li>• Exploded with a long-range TNT equivalent of 100 tons</li> <li>• Cloud ignited 6-8 minutes after release</li> </ul>
Hydrocarbons (liquid and gaseous)	Texas City, TX (7/21/79)	Refinery	Reflux accumulator line failed.	\$37 million	Alkylation unit, FCC unit, and control building sustained heavy structural damage.	• Windows broken half mile away	<ul style="list-style-type: none"> <li>• 4,000 to 5,000 gallons of liquids were discharged</li> <li>• Vapor cloud travelled 640 feet</li> <li>• Ignition occurred 2 minutes after initial release</li> </ul>
Hydrogen	Grangemouth, United Kingdom (3/22/87)	Refinery	Separator overpressurized, allowing release through relief valve.	\$88 million	Separator exploded and disintegrated.		• Projectile weighing 3 tons thrown 3,300 feet
Hydrogen	Richmond, CA (4/10/89)	Refinery	Failure of pipeline at a weld led to a leak of gas, resulting in a high-pressure fire	\$93.6M	Loss of 25 percent of refinery's throughput capacity; interruption of gas oil hydrocracker operations for 5 months		• Affected line at 2,800 psi
Hydrogen and Hydrocarbons	Martinez, CA (9/5/89)	Refinery	Failure of line downstream from a separator at a hydrotreater unit led to vapor cloud release, resulting in fire or explosion	\$52M	Destruction of hydrotreater unit		
Isobutane	Lake Charles, LA (8/8/67)	Refinery	Repairs to corroded valve further stressed the valve and increased the size of the leak; valve bonnet blew off.	\$63 million	One alkylation unit destroyed. Six cells of main cooling tower wrecked. Spheres ruptured, cone roof tanks caught fire.	• Windows broken six miles away	<ul style="list-style-type: none"> <li>• 17,500 gallons of isobutane released</li> <li>• Vapor cloud size estimated at 300 feet x 800 feet x 20 feet</li> <li>• Ignition 10-15 minutes after spill</li> </ul>
LPG	Mexico City, Mexico (11/19/84)	Terminal	Sphere ruptured while receiving product; incoming flow could not be shut off.	\$23 million	Four spheres and 44 bullets ruptured.		<ul style="list-style-type: none"> <li>• Product received at 341 psig</li> <li>• Initial ignition occurred 10 minutes after vapor cloud formed</li> <li>• Five minutes after initial ignition, series of BLEVEs erupted</li> <li>• Fireball estimated to be 1,200 feet in diameter</li> <li>• Projectiles weighing 20 tons were thrown 3,900 feet</li> </ul>
LPG	Rio de Janeiro, Brazil (3/30/72)	Refinery	Operator left LPG drain valve open.	\$13 million	All 21 tanks were destroyed; refinery facilities and buildings sustained blast damage.		• LPG initially released at 156 psi; relief valve release occurred at 239 psi

Chemical	Incident	Type of Facility	Cause/Description	Damage	Consequences		Other Factors About Explosion
					On-site	Off-site	
Methyl-tertiary-butyl-ether, propylene oxide, or styrene	Channelview, TX July 5, 1990	Petrochemical Plant	Explosion in giant holding tank occurred during maintenance. Source of ignition is unknown.	\$90 million	Deaths included five ARCO employees, one independent truck driver, and 11 non-union employees. The explosion leveled an area the size of a city block.		<ul style="list-style-type: none"> <li>•The fire sent a huge cloud of black smoke into the air that was visible 6 miles from the blast.</li> <li>•The clouds of smoke moved away from residential areas.</li> </ul>
Nitromethane	Starlington, LA May 1, 1991	Nitroparaffin Plant	Fire near a compressor detonated nitro methane.	\$110 million	Severely damaged the Angus facility. Debris included masses of twisted metal tanks and pipes.	<ul style="list-style-type: none"> <li>• Destroyed much of the town's main business district.</li> <li>• 20 families were left homeless.</li> <li>• Homes, hospital, and commercial buildings were damaged.</li> <li>• Damage included broken windows, collapsed ceilings, fallen siding from houses, burned-out vehicles, and litter of twisted metal.</li> </ul>	<ul style="list-style-type: none"> <li>•500-600 residents were evacuated from the immediate area</li> <li>•1 to 2 minutes between "pop" on recycle compressor and detonation</li> </ul>
Propane	Borger, TX (1/20/80)	Refinery	Piping/vessel overpressured after plug froze on contact with propane.	\$49 million	Alkylation unit and boiler plant destroyed. Refinery shut down.		
Propane	Denver, CO (10/3/78)	Refinery	Pipe on stabilizer reboiler failed.	\$37 million	Catalytic polymerization unit destroyed, other refining units heavily damaged.		<ul style="list-style-type: none"> <li>•Vapor cloud ignited approximately 300 feet from point of release</li> </ul>
Propane	Mont Belvieu, TX (11/5/85)	Terminal	Human error resulted in breaking of a high-pressure gas pipeline, leading to vapor cloud release, with subsequent explosion and fire	\$44.8M	Total loss of electronic equipment and computers in fire which radiated heat and melted glass windows of facility; large loss of gas inventory		<ul style="list-style-type: none"> <li>•Line under 800 psi</li> <li>•Vapor cloud size estimated at 44 acres</li> <li>•Ignition occurred 4-5 minutes after release</li> </ul>
Propane	Port Arthur, TX (6/8/88)	Refinery	Major failure of pipeline led to vapor cloud release; ignition and resulting explosion led to additional pipe failures and fires	\$17.4M	Heavy damage to storage tanks and pipelines		
Propane	Port Hudson, MO (12/9/70)		Pipeline ruptured		Complete destruction of warehouse	<ul style="list-style-type: none"> <li>•Broken windows up to 5 miles away</li> </ul>	<ul style="list-style-type: none"> <li>•132,000 pounds of propane released at 942 psig</li> <li>•Vapor cloud covered 10 acres</li> <li>•Ignition occurred after 24 minutes</li> </ul>
Propane	Ras Tanura, Saudi Arabia (8/15/87)	Gas Processing Plant	Release attributed to a flange in a relief valve line.	\$67 million			<ul style="list-style-type: none"> <li>•1,900 barrels of propane were released</li> </ul>

Chemical	Incident	Type of Facility	Cause/Description	Damage	Consequences		Other Factors About Explosion
					On-site	Off-site	
Propane	Romeoville, IL (7/23/84)	Refinery	Cracked circumferential weld leaked propane.	\$144 million	MEA absorber column exploded, toppled power transmission tower. Pipelines sheared, water treatment tank ruptured.	•Broken windows up to 6 miles away	<ul style="list-style-type: none"> <li>•Propane released at 200 psi, 100°F</li> <li>•Projectile weighing 20 tons thrown 3,500 feet</li> <li>•500 barrels of propane-butane mix were released as a result of initial explosion</li> <li>•BLEVE resulted in one projectile travelling 500 feet and another travelling 600 feet</li> </ul>
Propane	Torrance, CA (11/24/87)	Refinery	Failure of treater in a refinery process unit exploded into and severed pipelines and flarelines, resulting in multiple fires	\$16.8M	Extensive damage to the HF alkylation unit stripper, alumina treater, and depropanizer column		
Propane	Wood River (1/23/85)	Refinery	Ruptured pipe due to cold weather led to vapor cloud release, which ignited resulting in vapor cloud explosion	\$25.2M	Unspecified		
Propane and Propylene	Morris (6/7/89)	Petrochemical Plant	Power outage and operator error in venting propylene caused vapor cloud	\$41.6M	Extensive damage to 40 acres of production facility, including the ethylene production area		
Propane, Butane	Linden, NJ (3/20/79)	Refinery	Dead-end section of piping in FCC unit failed.	\$27 million	Unused control room destroyed; debris severed lines, releasing hydrocarbons.		•Vapor cloud 1.5 acres, 5-6 feet deep
Propane (C3 Hydrocarbons)	Norco (5/5/88)	Refinery	Internal corrosion in pipeline caused failure in pipeline elbow, which led to a vapor cloud release resulting in a major explosion with damage both on and off-site	\$327M	Severe and extensive damage to majority of refinery; fluid catalytic cracking unit was demolished and new one will be built	5,200 property claims received for damages up to 6 miles away	<ul style="list-style-type: none"> <li>•20,000 pounds of propane were released</li> <li>•Ignition occurred 30 seconds after release</li> <li>•Depropanizer column at 270 psi and 130°F</li> <li>•Overpressures up to 10 psi withing 100 meters</li> </ul>
Propylene	East St. Louis, IL (1/22/72)		Railroad cars collided and propylene released into vapor cloud; a second explosion also occurred.			•School, located 1 kilometer from explosion, suffered internal damage.	<ul style="list-style-type: none"> <li>•53.5 tons released</li> <li>•TNT equivalent (long-range) of 1-2.5 tons</li> <li>•Vapor cloud covered 5 acres</li> <li>•Ignition 5 minutes after release</li> </ul>

Chemical	Incident	Type of Facility	Cause/Description	Damage	Consequences		Other Factors About Explosion
					On-site	Off-site	
Propylene	New Castle, DE (10/21/80)	Petrochemical Plant	Operators removed valve.	\$64 million	Two process lines, the control building and the finishing area were severely damaged.		<ul style="list-style-type: none"> <li>•12,000 to 16,000 pounds of monomer released at 150 psi</li> <li>•Vapor cloud, 250 feet x 450 feet</li> <li>•Ignited after 1.5-2 minutes</li> </ul>
Propylene, hexane	Goi, Japan (10/8/73)	Petrochemical Plant	Operator opened wrong valve, releasing chemicals.	\$19 million			<ul style="list-style-type: none"> <li>•Vapor cloud ignited by a relay on an extruder 150 feet from point of release</li> </ul>
Propylene (other hydrocarbons)	Beek, Netherlands (11/7/75)	Petrochemical Plant	Leak caused by cold brittle fracture of a feed drum connection to the safety valve.	\$47 million	Storage tanks and buildings destroyed.	•2,310 cases of off-site damages	<ul style="list-style-type: none"> <li>•Three to five tons of hydrocarbon mist were released</li> <li>•Vapor cloud 100 meters in diameter, 1-2 meters high</li> <li>•Ignitions 2 minutes after release</li> <li>•TNT equivalent of 59 tons</li> </ul>
Styrene, vinyl chloride monomer	LaSalle, Quebec, Canada (10/13/66)	Petrochemical Plant	Reaction in mass polymerization out of control; rupture disc relieved.	\$11 million	A polystyrene building, an electric substation, and a warehouse destroyed. Rail car was knocked over.		<ul style="list-style-type: none"> <li>•1,500 lbs. of styrene were released and ignited</li> <li>•22,000 gallons of vinly monomer and 60,000-80,000 lbs. of additional styrene were ignited</li> </ul>
Vinyl, ethylacetylenes	Texas City, TX (10/23/69)	Petrochemical Plant	Heat-triggered decomposition.	\$27 million	Five towers destroyed or seriously damaged.		<ul style="list-style-type: none"> <li>•540 gallons of liquid hold-up ignited</li> <li>•Projectile of 800 lbs. travelled 3,000 feet</li> </ul>

## APPENDIX G

### CONTACTS WITH EXPERTS

Several experts were contacted for recommendations on models for flammables and for information on other issues related to flammables, such as vapor cloud explosions, accident scenarios, and potential consequences. Information acquired through discussions is presented for each expert individually.

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**Bob Benedetti**  
Flammable Liquids Engineer  
NFPA

Mr. Benedetti suggested that models are an inappropriate method for examining the consequences of a spill or pool fire on a community. He said that pool fires rarely leave the fence line of the facility.

Mr. Benedetti said that NFPA maintains a database on fires but a search for explosions is too general for the database. He also suggested that NFPA 30, the Combustible Liquid Code, might provide a good source of information for examining flammables. He said that these codes are basis for law in two-thirds of the states.

\* \* \*

**Dr. John Boccio**  
Department of Nuclear Energy  
Brookhaven National Laboratory

Dr. Boccio felt that one area that perhaps could be covered in somewhat more depth is, regarding flammable gases and liquids, the effects of propagation of the explosion into an area with obstacles, i.e., consequences of explosions on material structures, such as buildings. He said that we could probably find references in the literature to explosions in mine shafts.

Regarding the need to further validate the models of explosions included in our report, such as WHAZAN, etc., Dr. Boccio's view is that these models have been developed by established and credible organizations, and are widely used in industry, hence he wonders if the effort expended in further validating them would be a worthwhile one.

He also mentioned that DOE has shown an interest in developing their understanding of the hazards posed by explosive, flammable, and reactive chemicals, and that perhaps, at some point in the future, both the interests of EPA and DOE might be served by some sort of collaborative effort on this topic. He referred us to work being done in DOE's Office of Environmental Health.

\* \* \*

**David V. Eberhardt**  
Senior Engineer and Hazard Analyst  
Rohm & Haas Co.

Mr. Eberhardt was very well acquainted with the operation of the PHAST model for performing consequence analysis for flammable chemicals. He suggested that PHAST is the best model for screening hazards, and examining the impact of preventable releases such as line ruptures, accidental releases, BLEVE's, leaks and vents.

The PHAST model is a user friendly, PC based, modeling program designed jointly by Rohm & Haas Co. and Technica International, LTD of Columbus, Ohio at (614)848-4000 or (714)447-9400 in Los Angeles. Mr. Eberhardt said that Rohm & Haas Co. uses the PHAST model to screen accident scenarios. If by using the PHAST model the accident is shown to go beyond the fence line, the accident scenario is examined further using a sophisticated risk assessment model operated on a mainframe.

The PHAST model is easily operated. It is a menu driven program which also includes the ability to input specific parameters to tailor the model to the user's needs. Mr. Eberhardt said that Rohm & Haas Co. has used the PHAST model for vapor cloud dispersion, vapor cloud fires, and vapor cloud explosions (VCEs). It has been used to study the velocity of atomized material and travel distances for droplets. One useful feature that Mr. Eberhardt suggested was the coupling of accident scenarios (e.g., BLEVE's) which can be done with the PHAST model.

Mr. Eberhardt suggested that a Technica International user's group would be an excellent source of information regarding the operation of the PHAST model. Since Technica International operates a larger consequence model, updates are made to the PHAST program first, and general comments regarding the changes are solicited. This ensures that the PHAST model is extremely-up-to-date. Mr. Eberhardt said that changes are made to the PHAST model about twice a year.

\* \* \*

**Mike Johnson**  
PHAST Program Manager  
Technica International

Mr. Johnson answered questions related to the PHAST model, including technical questions related to model operation, source of the equations used in the models, and overpressure levels used PHAST. He also discussed the differences between PHAST and WHAZAN.

\* \* \*

**Dr. Marvin D. McKinley**  
Professor of Chemical Engineering  
University of Alabama

As far as a state-of-the-art model for performing consequence analysis for flammable chemicals, Dr. McKinley has heard positive feedback about the PHAST model developed by Technica International and Rohm & Haas.

Dr. McKinley is an expert on explosions of LPG and natural gas. He believes that EPA analysis should focus on the liquified gases as a source of VCE. Also, EPA assumptions in the consequence analysis need to reflect reality. NFPA and several states have regulations and codes that begin to address the dangers of VCE. He feels that industry follows these codes and regulations and that the specifications found in these codes (e.g., separation distances) should form the basis of EPA's assumptions in the consequence analysis. For example, if an NFPA code specifies that propane tanks should be 50 feet away from the property line, EPA should measure all overpressures at 50 feet. Dr. McKinley also feels that EPA needs to consider the conditions under which the flammables are used and stored in order to estimate the possible release quantities of flammable gases.

Concerning overpressures, Dr. McKinley agrees with Dennis Wade from Monsanto that EPA must first consider overpressures that can damage buildings - and thereby kill and injure people - before considering overpressures that can directly harm people. Concerning thermal exposure assumptions, Dr. McKinley believes that there needs to be a better combination of time and exposure for BLEVEs. Also, EPA should look into diking requirements when examining pool fire scenarios.

The rocketing of containers (e.g., projectiles) was not a great concern for Dr. McKinley. Even with BLEVEs, he felt that firefighters have enough time to cool the vessel thereby preventing the possibility of projectiles from an explosion. In fact, he doesn't see much chance of BLEVEs today.

Concerning accident scenarios, Dr. McKinley has found that most explosions of flammable chemicals result from a worker failing to follow procedures or ignoring existing information about hazards. For example, many explosions occur when someone fails to inert a tank previously filled with an flammable chemical and another person attempts to weld the tank. For additional scenarios, Dr. McKinley suggests we consult NFPA's Fire Journal Magazine for descriptions of incidents involving flammable chemicals. Also, he suggests we contact Dr. Grelecki for information on test data.

\* \* \*

**Dr. Dennis Wade**  
Manager of Safety Technology (Retired)  
Monsanto Co.

Dr. Wade has specific concerns that he believes were not adequately addressed in the Science Advisory Board Meeting. Dr. Wade feels that the greatest danger from flammable chemicals is the threat of explosions and not fires. Nobody has died in the community from thermal radiation resulting from ignition of flammables. However, the overpressure from a vapor cloud explosion may cause death or injury to the community. Also, he believes that EPA should focus on overpressures that cause a building to collapse rather than on overpressures that directly result in a death or injury. Historically, secondary effects such a building collapse have caused more deaths and injuries. Dr. Wade used the explosion in Pampa, Texas to support his opinion.

Dr. Wade recognized that there is a problem in trying to relate quantity of a release of flammable chemicals and the overpressure created by the explosion. He has some reservations about the WHAZAN and ARCHIE models because of the assumptions in those models. He also disagrees with EPA's consideration of 50% lower flammability limit. To gather information on state-of-the-art models for consequences of flammable explosions, Dr. Wade suggests three organizations:

AIChE Center for Chemical Process Safety - a committee of experts is working on models and guidelines in the area of vapor cloud explosions

Bureau of Industrial Safety (TNO) of the Netherlands - reissued the Yellow Book

Christian Michelson Institute -

Dr. Wade suggests that the models need to be reality tested with credible input and validated with test data. Examining accident scenarios can be helpful. Also, he suggests that EPA contact John Davenport, a world expert on data from vapor cloud explosions. Mr. Davenport is with Industrial Risk Insurers (Hartford).

The flammable chemicals considered in the consequence model should be those that are volatile at atmospheric pressure (e.g., propane, propylene). Other chemicals that must be heated to volatilize are less important to consider.

The trigger quantity must be large enough to create a vapor cloud. Monsanto used 15,000 pounds as a danger quantity, however, based on new data, the quantity has been reduced to 7,000 pounds.

Dr. Wade believes that one important scenario has not been adequately addressed - flammables in a closed building. This scenario combines the hazards of concentrated flammable vapors in a confined space, the possible large number of persons working in a building, and the issue of projectiles. In addition, EPA should look into the dangers posed by flammables at the retail and distributing level, rather than just the chemical manufacturing level.

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**Dr. Chesler Grelecki**  
Hazards Research Corporation

Dr. Grelecki presented an overview of fire and explosion hazards at a meeting at EPA. He also reviewed documents related to fire and explosion hazards, as well as answering questions and providing information to EPA in a conference telephone call discussing fire and explosion hazards.



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