The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and that elucidate difficult concepts. Manuscripts should not exceed ten double-spaced pages if possible and should be accompanied by the originals of any figures or photographs. Please submit them to Professor James O. Wilkes (e-mail: wilkes@umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

BOILING-LIQUID EXPANDING-VAPOR EXPLOSION (BLEVE)

An Introduction to Consequence and Vulnerability Analysis

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The chemical engineering curriculum should include information on safety, health, and loss prevention in the chemical industries.[1-4] A special sensitivity has developed in the industry as a result of the real possibility of accidents of catastrophic proportions, such as

- *The Flixborough accident (1974) at the Nypro plant in the United Kingdom when an unconfined vapor cloud explosion of cyclohexane resulted in 28 deaths and hundreds of injuries.*
- *The Sevesso (Italy, 1976) accident, where a runaway reaction caused toxic emissions of dioxin and methyl isocynate that caused animal deaths, dried vegetation, and affected 2000 people.*
- *The Bophal (India, 1984) accident, which is the greatest industrial disaster in the world to date, with about 2,500 deaths and between 100,000 and 250,000 injuries.*
- *The Mexico (1984) accident at St. J. Ixhuatepec where a BLEVE (Boiling Liquid Expanding Vapor Explosion) of a storage tank of LPG produced more than 500 deaths and 4,500 injuries.*

After the Sevesso accident, developed countries established compulsory legislation regulating declarations of risk by industry,[5] developed emergency plans inside plants and in the surrounding areas, and created coordinating organizations for emergency events. In the European community, the Sevesso I (formerly) and the Sevesso II (currently) directives cover

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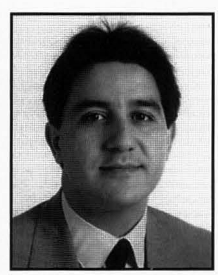

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Universities should act as a mirror for society, and during the past few decades the chemical engineering curriculum has made an effort to develop awareness of safety, health, and loss prevention, but there is still a need for greater awareness.

such actions, while in the United States, legislation has required development of both external and internal emergency plans. OSHA has published laws regarding industrial health and safety for the last thirty years, while other federal agencies, such as EPA, DOE, DOT, and associations such as API and AIChE, have developed their own legislation and codes for good practice.

Universities should act as a mirror for society, and during the past few decades the chemical engineering curriculum has made an effort to develop awareness of safety, health, and loss prevention, but there is still a need for greater awareness. The Center for Chemical Process Safety (CCPS), created in 1985, is an industry-driven center affiliated with the American Institute of Chemical Engineers (AIChE) that initiated a close relationship with engineering schools in 1992 by creating the Safety and Chemical Engineering Education program (SACHE). It provides teaching materials and programs that bring elements of process safety into the curriculum <http://www.aiche.org/sache/>. The AIChE <http://www.aiche.org/education/crsindex.asp> and the Institution of Chemical Engineers in the United Kingdom <http://www.icheme.org/she/tps/index.html> also provide a variety of safety courses for the chemical engineering curriculum. In Spain, a legislative article (R.D. 923/92) of the year 1992, established a degree of chemical engineering, and while some subjects on health and safety were included as obligatory, it is clearly insufficient.

To increase knowledge of safety during the undergraduate years of chemical engineering, several solutions have been proposed in the U.S.[6,7] The first proposal is to introduce an obligatory safety course, but that would increase the length of the curriculum and would be difficult for departments and ABET to agree upon. A second possibility, already incorporated in some programs, is to include safety courses as electives for undergraduates. The third proposal, perhaps more useful and easier to incorporate, is to give the students small "pills" of safety during their studies. One useful pill for showing students how to improve the safety of a process is the so-called "risk analysis." This technique gives a quantitative estimation of the risk involved in a given process.

In Spain, some knowledge of risk has been included as obligatory as a part of some courses on safety and/or health, and some universities have this program separated as elective options. For example, the University of Zaragoza has an elective course titled "Analysis and Risk Reduction in the Chemical Industry."

The objective of this article is to familiarize the student with risk analysis. The case selected for this is a boiling-liquid expanding-vapor explosion (BLEVE) of a tank truck of liquid propane. A brief introduction to consequence and vulnerability analysis models is included.

BRIEF DESCRIPTION OF THE CASE

A tank truck of 50 m^3 containing 19,000 kg of liquefied propane under its vapor pressure was discharging inside a factory. Due to unknown reasons, the tank developed a leak and propane gas discharged into the atmosphere. About five minutes later, some propane and oxygen (from the atmosphere) produced a mixture within the LFL (lower flammability limit) and the UFL (upper flammability limit). An unknown ignition source produced a weak explosion and started a fire close to the tank. The heat flux coming from the fire increased the temperature of the tank wall and the liquid propane within it. The liquid propane tracked its boiling point curve (p^0 vs T), substantially increasing the pressure in the tank. As a consequence, the tank ruptured catastrophically. This kind of phenomenon is a BLEVE (Boiling-Liquid Expanding-Vapor Explosion). At the moment of the accident, the ambient temperature was 36°C and the atmospheric pressure and relative humidity were 760 mm Hg and 41%, respectively.

The students should

- *Use consequence analysis models to study the possibility of a BLEVE occurrence and its effects (fireball radiation, damage due to overpressure) on the surrounding area.*
- *Use the Probit methodology for vulnerability analysis to speculate on the percentage of victims (deaths, injuries, etc.) for a given area.*

INTRODUCTION TO CONSEQUENCE ANALYSIS MODELS

STAGE 1

Is It Possible for a BLEVE to Take Place?

A BLEVE is the worst possible outcome when an LPG tank is exposed to fire. The possibility of a BLEVE occuring can be checked by using Reid's "massive nucleation theory."[9] This theory is based on the phenomenon of "spontaneous nucleation" that consists of a massive, instantaneous formation of tiny bubbles within the liquid mass, caused by a sudden depressurization of the vessel contents. When this phenomenon takes place, the possibility of a BLEVE occurs.

The zone of spontaneous nucleation can be seen in the pressure vs. temperature diagram shown in Figure 1. It represents the liquid-gas equilibrium as mathematically described by the appropriate Antoine equation for the material being used (*e.g.,* propane). (The equilibrium relationship, as well as the critical temperature and pressure for such material, can be obtained from the literature.[8]) From the critical point (*e.g.,* the critical temperature and pressure), a tangent line to the p^0-vs.-T curve must be traced up to a point where the ordinate represents the atmospheric pressure. The squared dot in Figure 1 shows the conditions inside the tank before the fire engulfment. As described by the Reid theory, every point located to the right of this imaginary vertical line (dashed and arrowed) that connects the above described tangent line at atmospheric pressure, is a suitable scenario for a BLEVE. This means that when the tank is exposed to a fire, the heat coming from it will increase the temperture (and correspondingly the pressure) inside the vessel, and the original conditions will begin to ascend, following the p^0-vs.-T curve. This progressive heating will lead to a point where the above-mentioned vertical line will be trespassed. Once this condition has been achieved, a sudden rupture of the vessel would lead to a BLEVE because of the sudden depresurization.

STAGE 2
Mathematical Models that Describe the Effects of BLEVEs

The literature describes three types of BLEVE effects: the shock wave (overpressure effects), the thermal radiation, and the fragment projection. This paper focuses on the shock wave and thermal effects as the main events in a BLEVE scenario.

Thermal Effects • The thermal effects of a BLEVE are related to radiation coming from the fireball. They are usually accounted for through empirical equations related to the quantity of substance involved in the BLEVE. Table 1 shows expressions that have been proposed by different authors to calculate the maximum diameter of the fireball, D_{max}[m], the duration of the fireball, t_{BLEVE}[s], and the height at the center of the fireball, H_{BLEVE}[m], as well as the results obtained with them for the given case.

The flow of radiation per unit of emissive surface area and time (I) in kW/m² can be calculated using

CCPS[10]

$$I = \frac{F_R(-\Delta H_{comb})M}{\pi(D_{max})^2 t_{BLEVE}} \qquad (1)$$

Elia model[12]

$$I = \frac{0.27\, M(-\Delta H_{comb})P_0^{0.32}}{\pi(D_{max})^2 t_{BLEVE}} \qquad (2)$$

Pape, et al., model[13]

$$I = 235\, P_v^{0.39} \qquad (3)$$

where F_R is defined as the ratio between the energy emitted by radiation and the total energy released by the combustion (the suggested value as stated in the literature[10] ranges from 0.25 to 0.4); $-\Delta H_{comb}$ is the heat of combustion of the material [kJ/kg]; P_0 is the initial pressure at which the liquid is stored [MPa]; and P_v is the vapor pressure of the stored liquid [MPa].

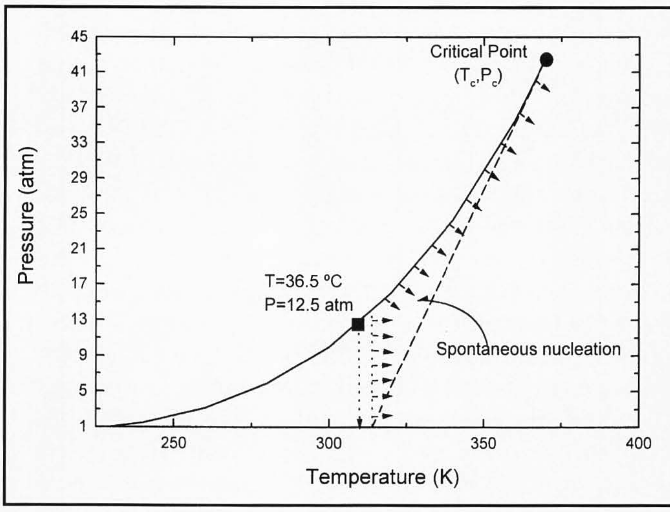

Figure 1. *Vapor pressure vs. temperature diagram showing the zone of spontaneous nucleation for propane, as described by Reid's Theory.[9]*

TABLE 1
Fireball Characteristic Parameters as Calculated by Different Authors
(M) Initial Mass of Flammable Liquid [kg]
(D_{max}) = maximum diameter of the fireball [m]
(H_{BLEVE}) = height at the center of fireball [m]
(t_{BLEVE}) = duration of fireball [s]

CCPS [10]	*CCPS [19]*
D_{max} = 6.48 $M^{0.325}$ = 159.3 m	D^*_{max} = 5.8 $M^{1/3}$ = 154.8 m
t_{BLEVE} = 0.825 $M^{0.26}$ = 10.7 s	t^*_{BLEVE} = 0.45 $M^{1/3}$ = 12 s
H_{BLEVE} = 0.75 D_{MAX} = 119.5 m	

TABLE 2
Flow of Radiation Per Unit of Surface Area and Time (I) for Different Models

	CCPS Model[10]	*Elia Model[12]*	*Pape, et al., Model[13]*
I(kW/m²)	336	301	306

Typical radiation values of fireballs associated with BLEVEs are quoted in the range of 200 to 350 kW/m^2. Taking a value of F_R = 0.325, the heat of combustion from reference 14, and the pressure inside the tank (1976 kPa) calculated as the vapor pressure of liquid propane at its superheat temperature (331 K using a Redlich-Kwong EOS approximation), the results are shown in Table 2. The value is inside the typical range for BLEVEs and close to the values reported by CCPS[10] (350 kW/m^2) for the intensity of radiation emitted by propane in BLEVE experiments.

The radiation received by a surface at a distance X from the emitting point can be calculated once the geometric view factor (F_{vg}) and the fraction of energy transmitted (atmospheric transmissivity, τ) are known:

$$I_R = I\tau F_{vg} \quad (4)$$

In this respect, when considering the vulnerability of people to the effects of a BLEVE, it is appropriate to use a geometric view factor corresponding to a surface perpendicular to a sphere:

$$F_{vg} = \frac{D^2}{4X^2} \quad (5)$$

Considering only the partial pressure of water present in the atmosphere at the moment of the accident, τ can be calculated approximately by[20]

$$\tau = 2.02(P_w X)^{-0.09} \quad (6)$$

where P_w is the partial pressure of the water at ambient temperature [Pa].

Another, simpler, model has been proposed by Roberts[11] where the intensity of radiation received by a surface at a distance X is given by an expression depending only on the mass of fuel:

$$I_R = 828\, M^{0.771} X^{-2} \quad (7)$$

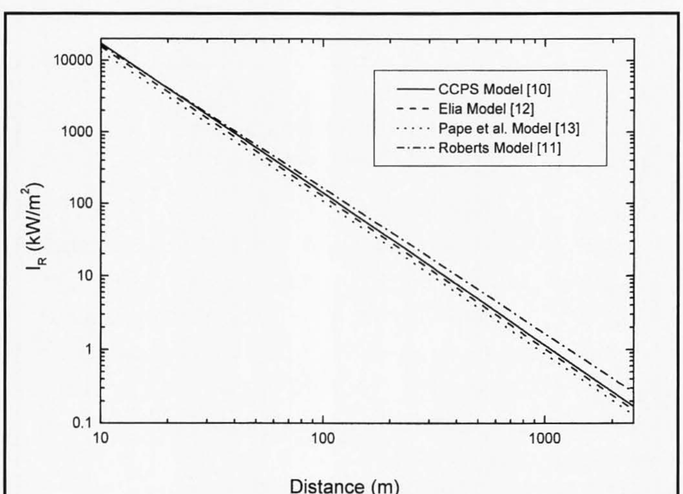

Figure 2. *Radiation received by a vertical surface as a function of distance.*

Overpressure Effects • Overpressures are difficult to predict in the event of a BLEVE. The vaporization and pressurization prior to the receptacle's collapse, and the duration of the rupture-depressurization, is extremely difficult to quantify. Experiments with explosives have demonstrated that the overpressure can be estimated using an equivalent mass of TNT. An approximate way to calculate the equivalent weight of TNT (W_{TNT}) for a BLEVE has been described by Prugh[15] as

$$W_{TNT} = 0.024\frac{PV^*}{k-1}\left[1-\left(\frac{1}{P}\right)^{\frac{k-1}{k}}\right] \quad (8)$$

where P is the pressure existing in the receptacle before the rupture [bar]. V* is given as

$$V^* = V_v + V_l\left(f\frac{D_l}{D_v}\right) \quad (9)$$

where V_v and V_l are the volumes of vapor and liquid [m^3] in the vessel before the explosion; D_l and D_v are the densities of liquid and vapor at the pressure and temperature of the system before the explosion; k is the ratio of Cp and Cv; and f is the fraction of liquid that flashes after depressurization. This can be calculated by the simple energy balance

$$f = \frac{m_v}{m_0} = 1 - e^{-\frac{Cp(T_0 - T_b)}{\Delta H_v}} \quad (10)$$

where m_0 and m_v are the initial mass of liquid and the amount vaporized in the flash, respectively, T_0 is the initial temperature, T_b is the normal boiling temperature, C_p is the heat capacity, and ΔH_v is the heat of vaporization. This expression to calculate f usually gives values on the order of two times smaller than those observed experimentally,[16] concluding that a flash fraction well above 20% might be considered as a total vaporization.

To calculate the equivalent TNT mass, the following data can be used:

- Liquid and vapor density are taken from reference 14
- Values for C_p (2.64 kJ/kg·K) and ΔH_v (430 kJ/kg) are taken from reference 5.
- Boiling temperature of propane at atmospheric pressure is 231 K

The value of f obtained with these data is 0.38. It has been mentioned that a more realistic value of the fraction that flashes is two times the value obtained with Eq. (10); therefore, the final estimation of f = 0.76 is close to 1. With f equal to 1, the equivalent TNT is 423.6 kg.

The TNT model is based on an empirical law established from trials using explosives.[17] This "cubic root law" establishes equivalent overpressure effects for explosions occurring at the same normalized distances, expressed as

$$z = \frac{R}{\left(W_{TNT}\right)^{1/3}} \qquad (11)$$

where z is the normalized distance [$m \cdot kg^{-1/3}$] and R is the real distance [m]. The experimental relation between overpressure and normalized distance for unconfined explosions can be found in several references.[5,18] Figure 3 shows the overpressure profile along distance for the proposed scenario.

INTRODUCTION TO VULNERABILITY ANALYSIS

The objective is to calculate the vulnerability to persons or installations expressed as the number of individuals or installations that could possibly be affected to a certain level of injury because of an accident. A possible method for estimating vulnerability consists of relating the dose received with the effect considered. This can be achieved from empirical evidence showing that individuals who have been subjected to a certain dose of the injuring agent (*e.g.,* a certain radiation intensity level during a given time) have suffered a particular effect (*e.g.,* death by burn). Therefore, the methods that relate causes directly with effects are hardly used, and the approximations to the problem of estimation of vulnerability generally follow a probabilistic approach. The Probit scale is a way of dealing with such approximations. The connection between Probit units (Y) and probability (P) is given by

$$P = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{Y-5} e^{-\frac{u^2}{2}} du \qquad (12)$$

The result of this expression is the Probit distribution with mean 5 and variance 1. The curve relating percentages and Probit units is shown in Figure 4.

Given the characteristics of the Probit variable, the following relationship can be written

$$Y = k_1 + k_2 \ell n V \qquad (13)$$

where Y is the number of Probit units, k_1 and k_2 are empirical constants depending on the causative factor and the level of damage to be analyzed, and V measures the intensity of the damage causative factor. The way in which V is expressed depends on the type of effect studied. Table 3 shows some values of the empirical constants (k_1 and k_2) and the expression related with V.

The Probit expressions for prediction of the effects produced by a given radiation intensity level during a given time use a causative factor, V, proportional to the product $t \cdot I_R^{4/3}$ (t is the exposure time and I_R is the intensity of radiation level). Regarding vulnerability to explosions, V is the

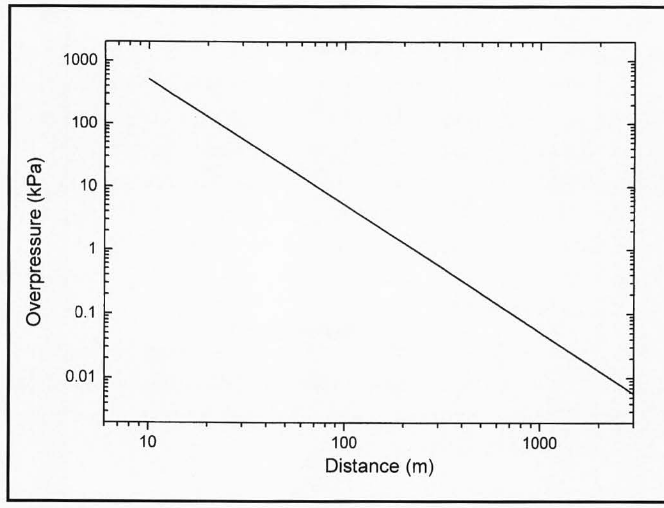

Figure 3. *Overpressure along distance for the BLEVE proposed scenario.*

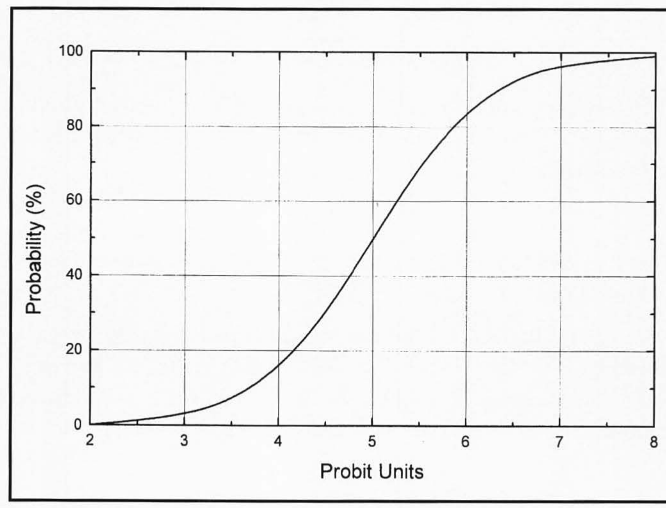

Figure 4. *Probability and Probit units relationship.*

TABLE 3
Probit Correlations for a Variety of Causes and Effects[18,21]

Cause	Effect	k_1	k_2	V
Explosion	Lung hemorrhage	-77.1	6.91	Overpressure peak(1)
Explosion	Eardrum rupture	-15.6	1.93	Overpressure peak(1)
Explosion	Structural damages	-23.8	2.92	Overpressure peak(1)
Explosion	Glass breakage	-18.1	2.79	Overpressure peak(1)
Thermal effects	Mortality	-38.5	2.56	$I_R^{4/3} * t$(2)
Thermal effects	Second-degree burns	-39.8	3.02	$I_R^{4/3} * t$(2)
Thermal effects	First-degree burns	-43.1	3.02	$I_R^{4/3} t$(2)

(1) Overpressure expressed in [Pa]
(2) I_R the intensity of radiation level received [W/m^2] and t the exposure time [s]

overpressure at a given point.

Figure 5 shows the percentage of people and installations affected by different effects and causes. The values of overpressure and radiation intensity received by a surface at a distance X (Elia model) obtained in the previous section (consequence analysis models) were used; the exposure time was taken as t_{BLEVE} obtained with the Elia model.[12] Table 4 shows the estimated distances at which 1% and 50% of the population or structures can be affected by a given effect. The limit at which 1% of the population may die is called "mortality threshold."

CONCLUSIONS

Risk analysis of major accidents is a useful tool for future chemical engineers; it gives not only a quantitative estimation of the risk involved in a given process, but also a suitable method for estimation of possible victims (environment, persons, and properties). A boiling-liquid expanding-vapor explosion (BLEVE) of a tank truck of liquid propane has been used to demonstrate this technique, and the blast and thermal effects have been calculated with several methods. The vulnerability of persons and/or installations affected in both cases has been calculated using the Probit methodology.

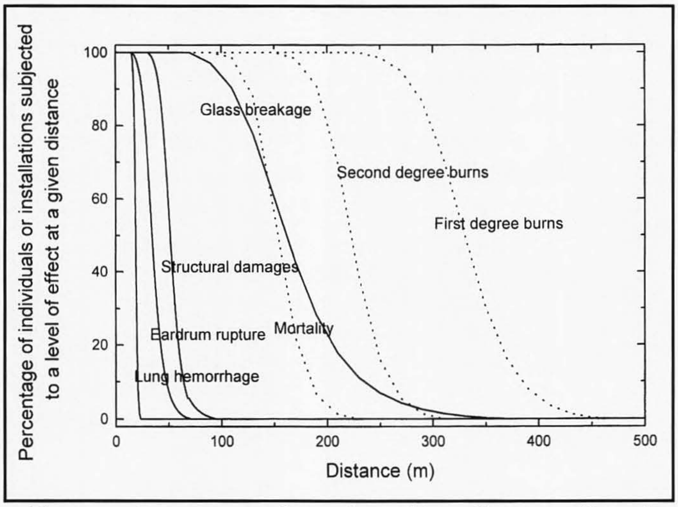

***Figure 5.** Percentage of people and installations affected by different effects and causes at a given point: overpressure effects (solid line) and thermal effects (dotted line).*

TABLE 4
Distance at which 1% and 50% of the Population (People or Objects) are Affected

Cause	Effect	Distance [m] 50%	Distance [m] 1%
Explosion	Lung hemorrhage	18.8	22.3
Explosion	Eardrum rupture	34.4	63.0
Explosion	Structural damages	51.6	84.7
Explosion	Breakage of glass	162	321
Thermal effects	Mortality due to thermal radiation	153	212
Thermal effects	Second-degree burns(1)	222	293
Thermal effects	First-degree burns(2)	329	436

(1) Epidermis and part of the dermis are burned
(2) A superficial burn in which the top layer of skin (part of the epidermis) has been slightly burned

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