Calculating the Explosion Energy of a Boiling Liquid Expanding Vapor Explosion Using Exergy Analysis

Russell A. Ogle, Juan C. Ramirez, and Suzanne A. Smyth
Exponent, Inc., 1011 Warrenville Road, Suite 215, Lisle, IL 60532; jramirez@exponent.com (for correspondence)

Following the work of Crowl on calculating the energy of explosions using exergy (thermodynamic availability), we examine the explosion energy of boiling liquid expanding vapor explosions (BLEVEs). A number of investigators have proposed schemes for calculating the maximum work that a BLEVE can perform on its surroundings. Their proposed evaluation schemes yield varying results because they depend significantly on the precise specification of the thermodynamic path taken by the vaporizing, expanding mass. We demonstrate how to evaluate the maximum theoretical work associated with a BLEVE as a function of the fluid's thermodynamic properties and its equation of state. Finally, we give numerical examples to compare the availability of a BLEVE with some of the proposed schemes suggested by others. The advantage of using exergy analysis to evaluate the maximum work of a BLEVE is based on the rigorous and unambiguous definition for exergy. © 2011 American Institute of Chemical Engineers Process Saf Prog 31: 51–54, 2012

Keywords: BLEVE, explosion, energy, exergy, availability, work

INTRODUCTION

An explosion is a release of energy that causes a blast wave [1]. The blast wave can cause injury and damage such as structural collapse or projection of missiles. The severity of an explosion is related to the magnitude of mechanical work that the blast can perform. For consequence analysis, it is useful to be able to predict the maximum work that can be done by the blast. There have been several efforts to calculate the maximum work of an explosion from thermodynamics. There are two basic approaches in determining the maximum work: the work method and the energy method. The work method depends on the specification of the thermodynamic path for the explosion (e.g., an isentropic or isothermal expansion). The energy method depends on specifying an energy function that represents the maximum work of the explosion. The energy method has the advantage in that it does not depend on the thermodynamic path: it depends only on the initial and final states.

Historically, explosion analysts have used either the internal energy or the Helmholtz free energy to calculate the maximum work of explosion [2–4]. However, in a series of three papers, Crowl [5–7] demonstrated that the thermodynamic availability or exergy was the better energy function for calculating the maximum potential work of an explosion. Crowl illustrated the explosion exergy concept for three primary cases: the sudden release of a compressed gas, a constant pressure deflagration, and a constant volume deflagration.

In this article, we extend Crowl's analysis to the boiling liquid expanding vapor explosion (BLEVE). Background section discusses the basic events of a BLEVE, outlines the thermodynamic models that have been previously recommended for evaluation of the explosion energy of a BLEVE, and introduce the exergy concept. The next section provides the basic results for the BLEVE of nonreactive fluids. Comparison of the Maximum Work Calculations section compares exergy calculations with maximum work calculations using the previously recommended thermodynamic models, and last section presents some conclusions.

BACKGROUND

Explosion Energy

A BLEVE results from the sudden loss of containment of a liquid heated above its normal boiling point. The loss of containment is usually the result of a catastrophic failure of the container or vessel holding the superheated liquid. There are two contributors to the BLEVE blast wave: (1) the compressed vapor in the container head space and (2) the vapor flashing from the superheated liquid. The magnitude of the blast also depends on the degree of superheat, that is, the temperature increment above the normal boiling point. As the degree of superheat increases, the fraction of liquid that flashes increases, thus increasing the severity of the blast. An assumption common to most of these models is that the flashing phenomenon is an adiabatic vaporization process, where the driving force for vaporization is the difference in the initial and final states of fluid enthalpy.

The question of how to calculate the explosion energy of a BLEVE has been addressed by a number of investigators. Prugh [8] discussed many aspects of BLEVE incidents and prescribed two methods for calculating the energy of explosion using a work method. His first method involved estimating the fraction of liquid flashed and then calculating the isentropic work of expansion for the combined volume of the original head space vapor and the flashed vapor. The vapor was assumed to obey the ideal gas equation of state. The expansion work was equated with the explosion energy.

Prugh's second method was an energy method. The second method equated the explosion work with the change in internal energy of the superheated liquid. This method also specifies a thermodynamic path (isentropic) for the vapor expansion. The expansion work is equated with the explosion energy. This was the method presented by the Center for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers (AIChE) [9].

Planas-Cuchi *et al.* [10] modified the energy method by equating the internal energy change of the superheated liquid to the irreversible work performed as the expanding vapor pushes against the surrounding atmosphere. Thus, unlike the first two methods discussed, the method of Planas-Cuchi *et al.* does not result in an estimate of the maximum potential work of the explosion. Abbasi and Abbasi [11] indicate that the explosion energy calculated by the method of Planas-Cuchi *et al.* may be as low as one-half of the value calculated by assuming an isentropic expansion. On the other hand, thermodynamic calculations that assume an isentropic expansion down to atmospheric pressure may result in final temperatures that are extremely, and improbably, cold compared to the natural environment.

Exergy Concept

Exergy, sometimes called the thermodynamic availability, is the maximum potential work that can be performed by a system as it comes to thermal, mechanical, and chemical equilibrium with the natural environment [12–14]. For a BLEVE, this means that the superheated liquid flashes from its initial state to its final state, where the final state is defined by the natural environment (ambient temperature and pressure).

Crowl [5–7] demonstrated the use of the batch exergy to calculate the maximum potential work from a compressed gas or a combustible fuel. By analogy, the explosion energy for a BLEVE is given by the batch exergy, where the subscript zero denotes the final (dead) state:

$$E = (U - U_0) + p_0(V - V_0) - T_0(S - S_0) \quad (1)$$

where E is the batch exergy (kJ/kg), U is the internal energy (kJ/kg), P is the absolute pressure (N/m^2), V is the specific volume (m^3/kg), T is the absolute temperature (K), and S is the entropy [kJ/(K kg)].

The dead state chosen for this analysis, designated by the subscript zero, is an ambient temperature of 25°C (298 K) and a pressure of one atmosphere (101.325 kPa).

It should be noted that Lienhard and his coworkers [15,16] have used exergy calculations to illustrate the damage potential of a metastable (superheated) liquid. However, their calculations were restricted to slightly superheated liquids undergoing an isobaric (constant pressure) process. Thus, their results are not directly applicable to the analysis of the BLEVE process, which is characterized by large degrees of superheat and significant changes in pressure.

To compute the batch exergy for a BLEVE, one final specification must be made: the initial temperature of the superheated liquid. In the spirit of determining the maximum potential work of the BLEVE, the temperature specification should be the maximum value that can be attained in the physical system. The maximum temperature that can be attained in a liquid heated at constant volume is the superheat limit temperature [17]. Values for the superheat limit temperature for many chemicals can be found tabulated in the literature or can be estimated from a cubic equation of state for the fluid. In the absence of thermodynamic data, the superheat limit temperature can be estimated as 90% of the value of the critical temperature [9].

EXERGY ANALYSIS OF THE BLEVE

Initially, we will consider only the thermomechanical energy released due to the change in states. The final state should be set at the ambient environmental conditions the fluid will be expanding into (i.e., the dead state). Choosing the initial state requires some analysis, but if no additional information is known about the system, the superheat limit temperature can be used to define the initial state. Once the initial and final states are thermodynamically defined, thermodynamic tables or software may be used with Eq. 1 to calculate the change in exergy of the system. Again, this is the maximum thermomechanical energy available in the system to do work.

For example, a liquid-full container of propane is assumed to BLEVE at 90% of its critical temperature, 332.9 K. The initial pressure will then be 2103.9 kPa based on the saturation pressure at that temperature. The internal energy, entropy, and specific volume can also be obtained for a saturated liquid at the initial temperature and pressure. The propane will expand into the environment, which is at standard temperature and pressure, setting the dead state properties as superheated propane vapor at 1 bar and 25°C. The maximum thermomechanical work, exergy, can then be calculated as follows:

$$E = (258.91 - 471.05) + 101^*(2.34 \times 10^{-3} - 0.55)$$
$$-298^*(0.9 - 2.22) = 120.9 \text{ kJ/kg}$$

This value of thermomechanical exergy is the maximum exergy attainable for the propane system. Lesser values of exergy are possible with smaller values of superheat.

The thermomechanical exergy is the estimate of maximum work for bringing a system from an initial state to thermal and mechanical equilibrium with its ambient surroundings. For systems that are chemically different from the surroundings (e.g., propane vs. the natural atmosphere), an additional term appears in the expression for total exergy. This additional term, the chemical exergy, is the work contribution that arises from bringing the system into chemical equilibrium with its environment. The chemical exergy is independent of the thermomechanical exergy; in other words, it is the work that can be performed by the difference in chemical potentials while the system is in thermal and mechanical equilibrium [18–20]. In the absence of chemical reactions, the chemical exergy is simply the diffusion exergy, analogous to (but not the same as) the minimum work of separation. For a blast wave to perform mechanical work against a structure, the blast wave must exert an overpressure, that is, the absolute total pressure (static plus dynamic pressure) must be greater than the atmospheric pressure. Thus, the diffusion exergy of the expanding fluid cannot contribute to the mechanical work performed by the blast wave. As the diffusion exergy cannot be used to produce useful work, this term can be omitted in calculating the maximum work of the BLEVE.

COMPARISON OF THE MAXIMUM WORK CALCULATIONS

This is a comparison of maximum work calculations for different chemicals. First, the chemicals are compared with each other to show how the magnitude of the BLEVE exergy depends on the thermodynamic properties of the chemicals. Finally, the different methods for calculating the maximum work are compared. The chemicals were selected to illustrate a range of thermodynamic properties and represent either a practical BLEVE hazard or have been the subject of laboratory study. Some of the pertinent properties for these chemicals are listed in Table1.

As discussed above, the initial and final (dead) states must first be defined to calculate the thermomechanical explosion

Table 1. Selected thermodynamic properties.

	Normal Boiling Point (K)	Critical Temperature (K)	Critical Pressure (kPa)
Propane	231.1	369.8	4,247
Chlorine	239.2	416.9	7,980
Ammonia	239.8	405.5	11,350
Water	373.2	647.3	22,120
R134a	246.9	374.1	4,060

Table 2. Work calculated by various methods.

	Exergy (kJ/kg)	Prugh (kJ/kg)	CCPS (kJ/kg)	Planas (kJ/kg)
Propane	120.9	67.8	68.8	26.1
Chlorine	74.5	52.3	41.6	14.1
Ammonia	351.0	135.1	157.0	64.9
Water	391.5	216.5	263.5	73.3
R134a	45.5	22.4	28.6	11.2

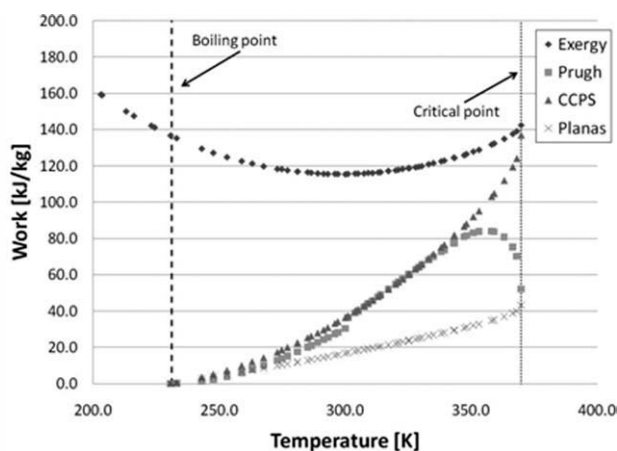**Figure 1.** Work calculated for propane.

energy of a BLEVE using exergy. The dead state was set at an ambient temperature and pressure of 25°C and 1 bar, respectively. For the purposes of illustration, five common fluids have been chosen for comparison: propane, water, chlorine, ammonia, and R134a. For each fluid, the initial state for a liquid-full container was set at 90% of the critical temperature of the fluid. The results are shown in Table 2.

Water produces the highest exergy with 391.5 kJ/kg, while the refrigerant R134a shows the lowest potential for work with 45.5 kJ/kg.

The methods presented by Prugh [8], the CCPS [9], and Planas-Cuchi *et al*. [10] discussed above for calculating the energy of a BLEVE were compared with the results for exergy. The results for an initial temperature of 90% of the critical temperature are shown in Table 2. At this point, the maximum work found via exergy is as large as twice the predicted energy of the other three methods. It is worth noting that the relative magnitudes of the methods are not consistent between the fluids. To explore this more closely, the calculations were performed over a range of initial temperatures.

Figure 1 shows the work calculated over a range of initial temperatures for propane. The exergy method consistently yields the highest values of work calculated, and it is worth examining the relative differences for the different methods at different initial temperatures. At low initial temperatures, the disparity between the work calculated by the exergy method and the other methods is greatest. However, as the initial temperature approaches the critical temperature of the fluid, the CCPS method [9] and the exergy method become increasingly similar. Prugh's method [8] begins to diverge from the CCPS method [9] at approximately 95% of the critical temperature, which is due to the failure of the ideal gas model near the critical point. The Planas-Cuchi *et al*. method [10] consistently provides the lowest magnitude of work, which is expected as it is not intended to produce the maximum.

Chlorine (not shown for brevity) produces similar results to propane with a greater difference between the Prugh [8] and CCPS [9] methods. Ammonia and R134a produce similar

results to propane and chlorine. The results for water differ noticeably from the propane and chlorine results but are omitted here for succinctness. All four methods exhibit similar shapes and differ mainly in their relative magnitudes. The exergy, Prugh [8], and CCPS [9] methods are significantly closer in magnitude for water than for any of the other fluids considered.

The relative magnitudes produced by the various methods of calculating the work released during a BLEVE are highly dependent on both the fluid examined as well as the initial temperature assumed.

CONCLUSIONS

The energy of explosion is the maximum potential work that can be performed by the explosive system. There is some disagreement among previous investigators on how to calculate the explosion energy for a BLEVE. Following the work of Crowl, we have presented a method for calculating the energy of explosion using the concept of exergy. The method was illustrated for selected nonreactive fluids. The advantage of using exergy analysis to evaluate the explosion energy for a BLEVE is that exergy has a rigorous and unambiguous definition.

LITERATURE CITED

1. Center for Chemical Process Safety, Guidelines for Vapor Cloud Explosion, Pressure Vessel Burst, BLEVE and Flash Fire Hazards, 2nd ed., American Institute of Chemical Engineers, New York, 2010.
2. G.F. Kinney and K.J. Graham, Explosive Shocks in Air, 2nd ed., Springer-Verlag, New York, 1985, pp. 23–24.
3. D.A. Crowl and J.F. Louvar, Chemical Process Safety: Fundamentals with Applications, Prentice Hall, New Jersey, 1990, pp. 188–192.
4. S. Sandler, Chemical and Engineering Thermodynamics, 3rd ed., Wiley, New York, 1998, pp. 711–717.
5. D.A. Crowl, Using thermodynamic availability to determine the energy of explosion, Plant/Oper Progr 10 (1991), 136–142.
6. D.A. Crowl, Using thermodynamic availability to determine the energy of explosion for compressed gases, Plant/Oper Progr 11 (1992), 47–49.
7. D.A. Crowl, Calculating the Energy of explosion using thermodynamic availability, J Loss Prev Process Ind 5

(1992), 109–118.

8. R.W. Prugh, Quantitative evaluation of "BLEVE" hazards, J Fire Protect Eng 3 (1991), 9–24.

9. Center for Chemical Process Safety, Guidelines for Vapor Cloud Explosion, Pressure Vessel Burst, BLEVE and Flash Fire Hazards, American Institute of Chemical Engineers, New York, 1994, pp. 158–161.

10. E. Planas-Cuchi, J.M. Salla, and J. Casal, Calculating overpressure from BLEVE explosions, J Loss Prev Process Ind 17 (2004), 431–436.

11. T. Abbasi and S.A. Abbasi, The boiling liquid expanding vapor explosion (BLEVE): Mechanism, consequence assessment, management, J Hazard Mater 141 (2007), 489–519.

12. E.P. Gyftopoulos and G.P. Beretta, Thermodynamics: Foundations and Applications, Dover Publications, New York, 2005, pp. 400–414.

13. M.J. Moran and H.N. Shapiro, Fundamentals of Engineering Thermodynamics, 6th ed., Wiley, New York, 2008, pp. 329–364, 746–762.

14. A. Bejan, Advanced Engineering Thermodynamics, Wiley, New York (1988), pp. 111–144, 215–223, and 368–398.

15. J.H. Lienhard, Some generalizations of the stability of liquid–gas–vapor systems, Int J Heat Mass Transf 7 (1964), 813–817.

16. J.H. Lienhard, N. Shamsundar, and P.O. Biney, Spinodal lines and equations of state: A review, Nucl Eng Des 95 (1986), 297–313.

17. R.C. Reid, Superheated liquids, American Scientist, 64, 1976, 146.

18. E.E. Michaelides, The second law of thermodynamics as applied to energy conversion processes, Energy Res 8 (1984), 241–246.

19. J. Kestin, Availability: The concept and associated terminology, Energy 5 (1980), 679–692.

20. K.W. Li., Applied Thermodynamics: Availability Method and Energy Conversion. Taylor & Francis, Washington, DC, 1996, pp. 114–117.