# Thermal destruction of vessels with liquid upon heating 

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#### Abstract

A new engineering technique of calculating the heating and thermal destruction of vessels containing liquid under extreme thermal loading conditions is offered. The heating of the shell and the internal vessel volume is described on the basis of the thermodynamic approach. The pressure growth in a vessel is a result of gas heating and liquid evaporation. Stresses within the shell and its destruction conditions are determined, which allows predicting the critical time of destruction upon heating. The calculation and experimental data for pressure growth inside the vessel are in good agreement.


## 1. Introduction

Modern industry works with potentially hazardous materials that constitute a danger to the lives of workers, infrastructure and environment. The fire and explosion safety of vessels filled with process liquids during their storage, operation and transportation is a very important issue [1, 2].

A typical emergency situation occurs when vessels with liquids are involved in industrial fire. Fire causes heating of vessel walls and contents up to critical temperatures, an internal pressure growth due to gas heating and liquid evaporation, shell rupture and, consequently, leads to destructive effects [1, 2].

Liquefied petroleum gas (LPG) vessels are especially hazardous because they often explode upon heating. The theoretical and experimental aspects of this problem were considered by different researchers [3-9]. In order to reduce the vessel explosion risk and to develop prevention strategies, it is necessary to analyze the heat and mass transfer processes during heating and to provide protection of vessels with liquids subjected to extreme thermal loading of various origin, intensity and duration.

Since full-scale experiments are difficult to perform, a good solution of this task is the mathematical modeling of emergency situations. This would help in determining the critical failure conditions of thermally loaded vessels with regard to the initial vessel state, liquid properties and thermal loading parameters as well as in designing thermal protection of vessels.

The aim of this paper is to develop a new engineering technique of calculating the heating of the vessel with liquid to predict the pressure dynamics, critical shell rupture conditions and the time of vessel resistance to extreme thermal loading.

## 2. Physical formulation of the problem

Let us consider the local heating of a long cylindrical vessel of diameter $D$ with metal shell thickness $d$, which is partially filled with liquid. The cross-section of the vessel and its schematic heating are depicted in Figure 1. Shell zones 1,2 are subjected to external thermal stress along arc CBD defined by central angles $\beta_{1}, \beta_{2}$. Zone 1 contacts with gas 6 on the inside, and zone 2 contacts with liquid 5 . The outer shell side along arc $C A D$ (zones 3,4 ) is in heat exchange with the environment.


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Figure 1. Cross-section geometry and scheme of heating a vessel with liquid under local thermal loading.
Zones 1 -4 - vessel shell; 5 - liquid; 6 - vapor-gas mixture; line $A B$ - liquid-gas interface; $l$ - distance to a liquid level; arc $C B D$ - thermally loaded region; arc $C A D$ - region contacting with the environment; $\beta_{1}, \beta_{2}, \alpha-$ central angles of arc $C B D$ and liquid level $A B$.

The vessel is partially filled with liquid. The distance from the liquid level (line $A B$ in Figure 1 with central angle $\alpha$ ) to the upper point of the vessel is equal to $l(l=0$ corresponds to complete filling). The geometric characteristics of each region (volumes $V_{i}$ and surface areas $S_{i}, i=1-4$ ) are expressed through the initial parameters of problem $D, d, l, \beta_{1}, \beta_{2}, \alpha$, with areas $S_{i}$ referring to $R L$ and volumes $V_{i}$ referring to $R^{2} L$, where $R, L$ are the radius and length of the vessel.

The physics of the process is the following. The shell, liquid and gas inside the vessel are heated up under thermal loading. This causes partial evaporation of liquid, an increase in temperature and vaporgas pressure, and the stress growth in the shell. Once the limiting values of these parameters are achieved, the shell ruptures. We need to define the dynamics of the liquid and vapor phase parameters, temperature and stress within the shell, and the critical destruction conditions of the vessel under local thermal loading.

The formulated problem will be solved with regard to the following physical processes: heat exchange between the vessel shell and environment, liquid and vapor-gas mixture; radiation heat exchange between the shells and with the liquid; liquid evaporation. We assume that each region can be characterized by a temperature that depends only on time. Liquid evaporation occurs under equilibrium conditions and is determined by saturated vapor pressure. In order to obtain the upper bound for heating of the regions, we neglect the heat flux over the vessel shell. Its thickness is assumed to be much smaller than the vessel radius.

## 3. Mathematical formulation of the problem

The problem of determining the temperature of zones $1-6$ of the vessel with regard to the made assumptions reduces to the solution of the following system of ordinary differential equations:
$\rho_{s} c_{s} d \frac{d T_{s 1}}{d t}=\alpha_{e}\left(T_{e 0}-T_{s 1}\right)+\varepsilon_{s f}\left(q_{R}-\sigma T_{s 1}^{4}\right)+\alpha_{s g}\left(T_{g}-T_{s 1}\right)+\varepsilon_{s l} \sigma\left(T_{l}^{4}-T_{s 1}^{4}\right) F_{1-5}+\varepsilon_{s s} \sigma\left(T_{s 4}^{4}-T_{s 1}^{4}\right) F_{1-4}$,
$\rho_{s} c_{s} d \frac{d T_{s 2}}{d t}=\alpha_{e}\left(T_{e 0}-T_{s 2}\right)+\varepsilon_{s f}\left(q_{R}-\sigma T_{s 2}^{4}\right)+\alpha_{s l}\left(T_{l}-T_{s 2}\right)$,
$\rho_{s} c_{s} d \frac{d T_{s 3}}{d t}=\alpha_{e}\left(T_{e 0}-T_{s 3}\right)+\alpha_{s l}\left(T_{l}-T_{s 3}\right)$,
$\rho_{s} c_{s} d \frac{d T_{s 4}}{d t}=\alpha_{e}\left(T_{e 0}-T_{s 4}\right)+\alpha_{s g}\left(T_{g}-T_{s 4}\right)+\varepsilon_{s l} \sigma\left(T_{l}^{4}-T_{s 4}^{4}\right) F_{4-5}+\varepsilon_{s s} \sigma\left(T_{s 1}^{4}-T_{s 4}^{4}\right) F_{4-1}$,
$\rho_{l} c_{l} R V_{5} \frac{d T_{l}}{d t}=\alpha_{s l}\left(T_{s 2}-T_{l}\right) S_{2}+\alpha_{s l}\left(T_{s 3}-T_{l}\right) S_{3}+\alpha_{l g}\left(T_{g}-T_{l}\right) S_{5}+$

$$
\begin{equation*}
+\varepsilon_{s l} \sigma\left(T_{s 1}^{4}-T_{l}^{4}\right) F_{5-1} S_{5}+\varepsilon_{s l} \sigma\left(T_{s 4}^{4}-T_{l}^{4}\right) F_{5-4} S_{5}-Q R \frac{d m_{v}}{d t} \tag{5}
\end{equation*}
$$

$m_{v} c_{\nu v} R \frac{d T_{g}}{d t}=\alpha_{\mathrm{lg}}\left(T_{l}-T_{g}\right) S_{5}+\alpha_{s g}\left(T_{s 1}-T_{g}\right) S_{1}+\alpha_{s g}\left(T_{s 4}-T_{g}\right) S_{4}$,
$m_{v}=\frac{\mu_{v} V_{6}}{R_{A} T_{g}} f\left(T_{l}\right)$,
$p=p_{v}=f\left(T_{l}\right)=A T_{l} \exp \left(-B / T_{l}\right)$
$t=0: \quad T_{i}=T_{l}=T_{g}=T_{e 0} . \quad i=1-4$.
Here the notation is the following: $T_{s i}$ is the temperature of the vessel shell zones $(i=1-4) ; T_{l}, T_{g}$ are the liquid and gas temperatures; $T_{e 0}$ is the initial temperature of all regions and environment; $S, V_{5}, V_{6}$ are the dimensionless surface areas, liquid and gas volumes; $\rho$ is the density; $m_{v}$ is the mass of gas in region 6 (referred to $R^{2} L$ ); $c, c_{v}$ are the specific heat capacity of the material and gas at constant volume; $\alpha$ is the convective heat exchange coefficient; $\varepsilon$ is the emissivity factor; $\sigma$ is the StefanBoltzmann constant; $F$ is the angular coefficient of radiation heat exchange between regions; $Q$ is the heat of evaporation of liquefied petroleum gas; $\mu_{\mathrm{v}}$ is the molar mass of gas; $R_{A}$ is the universal gas constant; $p, p_{v}$ are the gas pressure and saturated vapor pressure in region $6 ; f\left(T_{l}\right)$ is the liquid vapor curve [10]. Subscripts $s, l, g$ are the shell material, liquid and gas; $e$ is the environment; $f$ is the fire; $s l$, $l g, s g, s s, s f$ are respectively the shell-liquid, liquid-gas, shell-gas, shell-shell and shell-fire interfaces.

Equation (1) in differential system (1)-(6) describes heat exchange of zone 1 with the environment and gas-vapor mixture with regard to fire heat flux as well as radiation heat exchange with zone 4 and surface of liquid 5. The terms in the right-hand side of equation (2) denote external convective heat exchange, thermal loading and internal heat exchange with the liquid. According to equation (3), zone 3 is in heat exchange with the environment and liquid. For zone 4, equation (4) takes into account the external and internal convective heat exchange, radiation heat exchange with zone 1 and liquid 5 . The latter is in heat exchange with all zones and regions; additionally, equation (5) accounts for liquid evaporation. Vapor-gas mixture heating is expressed in equation (6). The differential system is supplemented with equations (7) and (8) for the determination of vapor mass and pressure in region 6. Initial conditions (9) correspond to the equality of all temperatures $T_{e 0}$. Angular coefficients $F$ in radiation heat exchange between zones and regions are determined through the geometric parameters of the problem [11].

## 4. Calculation of stresses within the vessel shell

The vessel destruction conditions will be estimated by considering a problem on the determination of the vessel shell stress state under internal $p$ and external $p_{\text {out }}$ pressures uniformly distributed over the lateral surface. In view of axial symmetry, radial $\sigma_{r}$ and tangential (circumferential) $\sigma_{\varphi}$ stresses depend only on radius $r$; tangential stress $\tau_{r \varphi}=0$. The equilibrium equation for an elementary volume of the vessel shell reads [12]:

$$
\begin{equation*}
\sigma_{r}-\sigma_{\varphi}+r \frac{\partial \sigma}{\partial r}=0 . \tag{10}
\end{equation*}
$$

The stress and strain are related according to Hooke's law as follows [12]:

$$
\begin{equation*}
\sigma_{r}=\frac{E}{1-\mu^{2}}\left(\varepsilon_{r}+\mu \varepsilon_{\varphi}\right), \quad \sigma_{\varphi}=\frac{E}{1-\mu^{2}}\left(\varepsilon_{\varphi}+\mu \varepsilon_{r}\right) \tag{11}
\end{equation*}
$$

where $E, \mu$ are the Young's and Poisson's moduli, and $\varepsilon_{r}, \varepsilon_{\varphi}$ are the radial and tangential strains. Now let us write expressions that relate strains with displacement $u$ :

$$
\begin{equation*}
\varepsilon_{r}=\frac{\partial u}{\partial r}, \quad \varepsilon_{\varphi}=\frac{u}{r} \tag{12}
\end{equation*}
$$

After substituting equations (11), (12) into equation (10), we have:

$$
\begin{equation*}
\frac{d^{2} u}{d r^{2}}+\frac{1}{r} \frac{d u}{d r}-\frac{u}{r^{2}}=0 \tag{13}
\end{equation*}
$$

The general solution of equation (13) is written as

$$
\begin{equation*}
u=A r+\frac{B}{r} \tag{14}
\end{equation*}
$$

Constants of integration $A, B$ are found from boundary conditions:

$$
\begin{equation*}
\sigma_{r}\left(r_{\text {in }}\right)=-p, \quad \sigma_{r}\left(r_{\text {out }}\right)=-p_{\text {out }}, \tag{15}
\end{equation*}
$$

where $r_{\text {in }}$ and $r_{\text {out }}$ are the inner and outer radii of the vessel shell of thickness $d=r_{\text {out }}-r_{\text {in }}$. Hence we come to expressions for stresses $\sigma_{r}, \sigma_{\varphi}[12]$ :

$$
\begin{gather*}
\sigma_{r}=\frac{p r_{\text {in }}^{2}-p_{\text {out }} r_{\text {out }}^{2}}{r_{\text {out }}^{2}-r_{\text {in }}^{2}}-\frac{\left(p-p_{\text {out }}\right) r_{\text {in }}^{2} r_{\text {out }}^{2}}{\left(r_{\text {out }}^{2}-r_{\text {in }}^{2}\right) r^{2}}, \quad r_{\text {in }} \leq r \leq r_{\text {out }},  \tag{16}\\
\sigma_{\varphi}=\frac{p r_{\text {in }}^{2}-p_{\text {out }} r_{\text {out }}^{2}}{r_{\text {out }}^{2}-r_{\text {in }}^{2}}+\frac{\left(p-p_{\text {out }}\right) r_{i n}^{2} r_{\text {out }}^{2}}{\left(r_{\text {out }}^{2}-r_{\text {in }}^{2}\right) r^{2}}
\end{gather*}
$$

Since internal pressure is much higher than external pressure, $p \gg p_{\text {out }} p_{\text {out }}$ can be neglected. Hence equations (16) take on a simpler form:

$$
\begin{gather*}
\sigma_{r}=\frac{p r_{\text {in }}^{2}}{\left(r_{\text {out }}^{2}-r_{\text {in }}^{2}\right)}\left(1-\frac{r_{\text {out }}^{2}}{r^{2}}\right), \quad r_{\text {in }} \leq r \leq r_{\text {out }},  \tag{17}\\
\sigma_{\varphi}=\frac{p r_{\text {in }}^{2}}{\left(r_{\text {out }}^{2}-r_{\text {in }}^{2}\right)}\left(1+\frac{r_{\text {out }}^{2}}{r^{2}}\right) .
\end{gather*}
$$

Maximum stresses are on the inner shell side:

$$
\begin{gather*}
r=r_{\text {in }}: \quad\left(\sigma_{\varphi}\right)_{\max }=p \frac{\beta^{2}+1}{\beta^{2}-1}, \quad \beta=\frac{r_{\text {out }}}{r_{\text {in }}}  \tag{18}\\
\sigma_{r}=-p .
\end{gather*}
$$

Thus, $\left(\sigma_{\varphi}\right)_{\text {max }}$ increases with the growing internal gas pressure and decreasing shell thickness. According to energy theory of forming, the equivalent stress is [12]:

$$
\begin{equation*}
\sigma_{\mathrm{eqv}}=\frac{1}{\sqrt{2}} \sqrt{\sigma_{\varphi}^{2}+\sigma_{r}^{2}+\left(\sigma_{r}-\sigma_{\varphi}\right)^{2}} \tag{19}
\end{equation*}
$$

Destruction occurs when $\sigma_{\text {eqv }}$ achieves ultimate stress $\sigma_{u}(T)$ of structural material which depends on temperature. Substituting equation (18) into equation (19) yields:

$$
\begin{equation*}
\sigma_{\mathrm{eqv}}=p \sqrt{\xi^{2}+\xi+1} \geq \sigma_{u}(T), \quad \xi=\frac{\beta^{2}+1}{\beta^{2}-1} \tag{20}
\end{equation*}
$$

Calculated vapor pressure $p$ can be used to determine $\sigma_{\text {eqv }}$. By comparing it with ultimate stress $\sigma_{u}(T)$ of material (20), we can find the critical temperature and time of vessel explosion under thermal loading.

## 5. TNT equivalent of thermal destruction of the vessel

The estimation of the mechanical process of vessel destruction requires the knowledge of explosion energy, or TNT equivalent. The TNT equivalent is the measure of energy release expressed in the explosive quantity of trinitrotoluene (TNT) that releases the same amount of energy in detonation.

During destruction of a vessel with combustible gases and liquids, explosion energy $E_{\text {expl }}$, MJ consists not only of chemical energy of the matter, but also of potential energy of pressurized gas [13]:

$$
\begin{equation*}
E_{\text {expl }}=Q_{\text {liq }} M_{\text {liq }}+\frac{\left(p-p_{\text {out }}\right) V_{g}}{(\gamma-1)}, \tag{21}
\end{equation*}
$$

where $Q_{\text {liq }}, M_{\text {liq }}$ are the specific heat ( $\mathrm{MJ} / \mathrm{kg}$ ) and mass ( kg ) of combustible liquid, $p, V_{g}$ are the gas pressure (MPa) and gas volume $\left(\mathrm{m}^{3}\right)$ in the vessel at the moment of rupture, and $\gamma$ is the adiabatic exponent of gas.

If we equate vessel explosion energy $E_{\text {expl }}$ to explosion energy $E_{\mathrm{TNT}}=Q_{\mathrm{TNT}} G_{\mathrm{TNT}}$ of TNT of mass $G_{\text {TNT }}$, we can find the TNT equivalent:

$$
\begin{equation*}
G_{\mathrm{TNT}}=E_{\text {expl }} / Q_{\mathrm{TNT}}, \mathrm{~kg} \tag{22}
\end{equation*}
$$

where $Q_{\mathrm{TNT}}=4.52 \mathrm{MJ} / \mathrm{kg}$.

## 6. Numerical calculation results and their analysis

The proposed model was validated in modeling calculations for a steel liquefied petroleum gas vessel subjected to fire [8]. The vessel has diameter $D=0.3 \mathrm{~m}$, wall thickness $d=0.004 \mathrm{~m}$, volume $50 \mathrm{dm}^{3}$; it contains 21 kg of liquid propane [8]; the distance from the upper point to the liquid level $l=0.0651 \mathrm{~m}$; the vessel is fully involved in fire, $\beta_{1}=0^{\circ}, \beta_{2}=360^{\circ}$ (zones 3,4 in the scheme of heating are absent).

The initial parameters of the problem according to the data of papers $[3,8,10]$ are the following: thermophysical properties of the shell material and liquefied petroleum gas $-\rho_{s}=7800 \mathrm{~kg} / \mathrm{m}^{3}$, $\mathrm{c}_{s}=500 \mathrm{~J} /(\mathrm{kg} \cdot \mathrm{K}), \rho_{l}=500 \mathrm{~kg} / \mathrm{m}^{3}, \mathrm{c}_{l}=3000 \mathrm{~J} /(\mathrm{kg} \cdot \mathrm{K}) ;$ convective heat transfer $-\alpha_{e}=25 \mathrm{~W} /\left(\mathrm{m}^{2} \cdot \mathrm{~K}\right), \alpha_{s l}$ $=\alpha_{l g}=\alpha_{s g}=1200 \mathrm{~W} /\left(\mathrm{m}^{2} \cdot \mathrm{~K}\right)$; radiation properties of materials $-\varepsilon_{s f}=1.0, \varepsilon_{s s}=\varepsilon_{s l}=0.8 ;$ LPG evaporation characteristics $-A=6.0 \cdot 10^{6} \mathrm{~Pa} / \mathrm{K}, B=2259 \mathrm{~K}, Q=4.27 \cdot 10^{5} \mathrm{~J} / \mathrm{kg}$; initial temperature $T_{e 0}=7^{\circ} \mathrm{C}$; heat flux $-q_{R}=60 \mathrm{~kW} / \mathrm{m}^{2}$.

The system of ordinary differential equations (1)-(9) was solved numerically using an implicit difference scheme. Figure 2 gives the calculation results on heating an unprotected liquid propane vessel. Curves $1,2,5,6$ show the temperature of vessel regions, curve 7 is for the vapor pressure in region 6 , and the asterisks denote the experimental data for pressure obtained in full-scale testing [8].

As one can see, the most rapid heating is observed in shell zone 1 subjected to external heat flux and contacting with gas from the inside (curve 1). The temperature here reaches $\sim 200^{\circ} \mathrm{C}$ on the 200th second of the process. A less intensive heating occurs in zone 2 contacting with the liquid because a large part of heat in this zone transfers to the liquid due to intensive heat transfer. The gas mass in region 6 inside the vessel is most heated (curve 0 ). However, since gas exchanges heat with the liquid, its temperature is lower than the shell temperature in zone 1 . The large mass and high heat capacity of LPG determine a considerably lower liquid temperature (curve 5) with an almost linear dependence.

Pressure grows rapidly inside the vessel (curve 7). Its value reaches $\sim 60 \mathrm{~atm}$ on the 200th second of heating, which is due to an increase in the partial vapor pressure of liquid propane. The calculated and experimental data for pressure are in good agreement. This means that the mathematical model adequately describes the heat exchange and liquid evaporation because pressure integrally characterizes the thermodynamic state inside the vessel. The calculation results show that the pressure value strongly depends on the method of determining temperature at the gas-liquid interface which enters into equation (8). The heat losses on LPG evaporation influence insignificantly the thermal state of the liquid and gas.

According to equation (20), the pressure growth causes an increase in stress $\sigma_{\text {eqv }}$ within the vessel shell (Figure 3). Its upper bound from the physical standpoint is the ultimate stress of structural material (20). Then explosive vessel destruction occurs. Since ultimate stress $\sigma_{u}(T)$ of the steel shell decreases with the temperature growth, its lower bound is achieved during heating of shell zone 1 whose temperature is the highest. It is the zone where the vessel rupture is most probable.


Figure 2. Temperature of shell zones (1, 2), liquid (5), gas (6), and vapor pressure (7) for an unprotected vessel in fire.

*     - full-scale experiment, vapor pressure [8].


Figure 3. Time-dependence of equivalent stress $\sigma_{\text {eqv }}$ within the shell under heat flux of fire. $\sigma_{u}(T)$ is the ultimate stress of material. $t_{\text {crit }}$ is the critical time when vessel shell rupture begins.

Figure 3 shows curve $\sigma_{u}(T(t))$ calculated by the temperature of this zone (by curve 1 in Figure 2) for the steel shell. The abscissa of intersection of curves $\sigma_{\max }(t)$ and $\sigma_{u}(T(t))$ gives critical time $t_{\text {crit }}$ of shell rupture beginning, and the ordinate gives critical stress $\sigma_{\text {crit }}$. At the above-given initial data of the problem the critical parameter values are $t_{\text {crit }} \approx 240 \mathrm{~s}, \sigma_{\text {crit }} \approx 337 \mathrm{MPa}$. Using the data of Figure 2 and the obtained value of time $t_{\text {crit }}$, we can find critical values of pressure inside the vessel $p_{\text {crit }} \approx 91 \mathrm{~atm}$ and temperature $T_{i, \text { crit }}$ of shell zones 1 and 2 , liquid 5 , and gas 6 . Analysis of the obtained data demonstrates that the resistance time of an unprotected LPG vessel in fire with heat flux $q_{R}=60 \mathrm{~kW} / \mathrm{m}^{2}$ is insufficient for fire prevention measures, which points to the necessity of thermal protection.

Of practical interest is to estimate the potential energy of pressurized gas $E_{\text {press }}$ at the moment of vessel destruction (the second term in equation (21)). For the initial data of the problem we have pressure $p_{\text {crit }} \approx 9.1 \mathrm{MPa}, p_{\text {out }} \approx 0.1 \mathrm{MPa}$, volume of the vessel region with gas $V_{g}=0.0113 \mathrm{~m}^{3}$ at length $L=1 \mathrm{~m}$, and adiabatic exponent $\gamma \approx 1.1$ [10]. Calculations yield $E_{\text {press }} \approx 1.0 \mathrm{MJ}$, which corresponds to $\Delta \mathrm{G}_{\mathrm{TNT}} \approx 0.22 \mathrm{~kg}$ of trinitrotoluene according to equation (22).

## 7. Conclusion

1. A new engineering technique of calculating the heating and thermal destruction of vessels with liquid under extreme thermal loading conditions has been proposed.
2. The calculation and experimental data for pressure growth inside the vessel are in good agreement, which indicates that the model is able to adequately describe the heat exchange and liquid evaporation processes.
3. Analysis of the obtained data shows that it is necessary to provide proper thermal protection of LPG vessels to ensure their resistance against industrial fires.

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