A calculation of welded pressure vessels for fire safety is shown in this paper. At the first step, the temperature of the steel walls has been investigated, and the inner liquid pressure and the temperature increase. It is assumed that the safety valve is out of work and cannot reduce the increasing pressure. At the second step, the growing pressure and softening steel represent danger after a critical time. The result will be a safe time when the damage will occur. Three different alternatives have been calculated: the increase of the vessel wall thickness, the increase of the applied steel yield stress, the effect of the thermal coating. The thermal coating was the best alternative. This kind of calculation helps to find the best safe solution.
2 Calculation of a pressure vessel for fire

In the calculation, a vertical cylindrical container has been examined (Figure 3). We do not deal with the dimensioning of the vessel shed in this paper. The material stored is propane with a charge of 80%. The initial temperature is 294 °K, and the initial pressure is 0.856 MPa. The vessel height is \( L = 7 \) m, its outside diameter is \( d_{\text{ext}} = 3.2 \) m. We selected P235 steel in the container. The wall thickness \( s \) is determined by the boiler formulation Eq. (1), which is rounded to a sizeable plate size of 10 mm. In this formula, other than the checklist, the dimension \( p \) is MPa, \( d_{\text{ext}} \) and \( s \) dimension are mm. The list of symbols is at the end of the paper.

\[
s = \frac{p \cdot d_{\text{ext}}}{2 \cdot f_y / 1,5 + p} \quad [\text{mm}]
\]  

(1)
2.1 Geometric calculations

The calculations require for the determination of total 5 surfaces, using the following formulas:

### Table 1. Determination of the vessel's geometrical parameters [3].

<table>
<thead>
<tr>
<th>Surface Description</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>The inner surface of the contacting liquid</td>
<td>$A_{1\text{int}} = 2\pi (R_t - s)h_{liq} + \pi (R_t - s)^2$</td>
</tr>
<tr>
<td>The outer surface of the contacting liquid</td>
<td>$A_{1\text{ext}} = 2\pi R_t (h_{liq} + s) + \pi R_t^2$</td>
</tr>
<tr>
<td>The inner surface of the wall contacting to the vapor space</td>
<td>$A_{2\text{int}} = 2\pi (R_t - s)(L - h_{liq}) + \pi (R_t - s)^2$</td>
</tr>
<tr>
<td>The outer surface of the wall contacting to the vapor space</td>
<td>$A_{2\text{ext}} = 2\pi R_t (L - h_{liq} + s) + \pi R_t^2$</td>
</tr>
<tr>
<td>Liquid space vapor surface boundary</td>
<td>$A_{LV} = \pi (R_t - s)^2$</td>
</tr>
</tbody>
</table>

2.2 The equation system

The mathematical model consists of energy balances, mass balances, state equations and empirical correlations in the following way:

Energy balance for the liquid phase:

$$c_L m_L \frac{dT_P}{dt} = q_L + \frac{dm_L}{dt} (c_L (T_P - 273,15) + r)$$  \hspace{1cm} (2)

Fluid level change:

$$\frac{dL}{dt} = \frac{dm_L}{dt} \left( \frac{1}{\rho_L \pi R_t} \right)$$ \hspace{1cm} (3)

Mass balance:

$$\Delta m_L = -\Delta m_V$$ \hspace{1cm} (4)
Universal law of gas:

\[ pV = nRT \]  

(5)

Steam-liquid equilibrium curve for propane from Antoine equation (Appendix 2):

\[ p = f(T) \]  

(6)

Energy balance on the vessel wall:

\[
d_s \rho_s c_s \left( \frac{A_{int} + A_{ext}}{2} \right) \frac{dT}{dt} = \sigma \varepsilon_s (T_F^4 - T_T^4) A_{ext} + \\
+ \alpha_F (T_F - T_T) A_{ext} - \alpha_V (T_T - T_P) A_{2int} - \alpha_L (T_T - T_P) A_{1int}
\]  

(7)

Heat flow between vessel wall and liquid space:

\[ q_L = \alpha_L A_{1int} (T_T - T_P) + \sigma \varepsilon_L (T_T^4 - T_P^4) A_{2int} \]  

(8)

Heat flow between the vessel wall and the steam room:

\[ q_V = \alpha_V A_{2int} (T_T - T_P) \]  

(9)

Heat Transfer Factor between Vessel Wall and Steam Room: [3]

\[ \alpha_V = 3.41 (T_T - T_P)^{0.25} \]  

(10)

Heat transfer factor between the vessel wall and the liquid space [3]:

\[
\alpha_L = 0.138 \frac{k_L}{Z_L} \left( \frac{Z_L \rho_L g \beta (T_T - T_P)}{\mu_L^2} \right)^{0.36} \cdot \left( \frac{\varepsilon_L \mu_L}{k_L} \right)^{0.175} - 0.55 \]

(11)

Heat transfer factor between fire and wall [3]:

\[ \alpha_F = 25 \]  

(12)

2.3 Thermodynamic calculations

Calculations are done using the Eurocode regulations [4,5] and the Microsoft Excel and Solver extension. It is also well suited for solving iteration tasks. Since we solve the solution of the equations by the finite difference method, so at every single time we must run Solver, which is too time-consuming, so we made a simple Macro for the iteration. The time period selected is \( \Delta t = 5 \) seconds.

2.4 Standard fire curves

Real fires consist of three phases: growth, full development and repression. However, in most international standards, fire resistance times, refer to the behaviour during heating up, based on a specific temperature-time curve. These curves do not characterize the actual fires but provide a steadily decreasing rise in temperature at the same time [4, 6]. If a chemical vessel is in the fire, its source is certainly somehow hydrocarbon.
Therefore, instead of the standard ISO fire curve, a hydrocarbon fire curve has been used to calculate the temperature of the fire. Equation of which [5, 7] is:

\[
T = 20 + 1080 \left(1 - 0,325e^{-0,167t} - 0,675e^{-2,5t}\right)
\]  

(13)

\[\text{Figure 4. Hydrocarbon and ISO } 834 \text{ fire curves [4, 6].}\]

Figure 4 shows that after 7.5 minutes of fire, its temperature reaches 1000 °C, and after 30 minutes, it has reached 1100 °C and does not continue to rise. During the calculations, it is supposed that the vessel is completely blocked by the flame. Fire transmits heat to the vessel wall by heat transfer and heat radiation. The temperature rise of the container material is described in Equation 7. When the container is covered by fire, both the vessel material and the temperature of the charge rise. As a result, physical characteristics (density, specific heat, evaporation heat, yield stress, Young modulus, etc.) are constantly changing, making the calculation difficult. Changes in the physical properties of propane can be found in Annex 1. First, the different heat transfer factors have been determined from Eqs. (10-12), and the heat currents are calculated from Eqs. (8-9). In the second step, the iteration loop has been made is shown in Figure 5.

The temperature of the container and the charge is shown in Figure 6, depending on the time spent in the fire. The diagram indicates that for 15 minutes, the temperature of the propane rises up to 73.5 °C until the temperature of the vessel wall reaches 367 °C.

\[\text{Figure 5. Flow chart of the iteration.}\]
To determine the failure at wall temperature, the pressure increase in the container is significant, and on this basis, we can calculate the stress in the vessel wall as a function of time. Figure 7 shows the pressure change in the vessel. The initial pressure in the vessel is 0.856 MPa. After 15 minutes, the pressure increases by more than three times up to 2.76 MPa, in the diagram.

2.5 Stress calculations

2.5.1 Stress in the function of time

To determine the failure time, strength calculations are required. The vessel material is P235 steel with a yield stress of 235 MPa. Usually, this is the limit stress; if it exceeds the yield stress in the vessel wall, it will fail. With the increase of the temperature, the steel strength and stiffness characteristics are constantly decreasing at the pressure vessel. In the case of the vessel, however, we determine the yield stress, according to the temperature, based on the data provided by the manufacturer (Figure 8).
In the case of pressure vessels, the temperature rise and the stress in the vessel wall have been calculated. These parameters determine how the temperature can go up, how it can withstand the strain caused by the internal pressure.

The other factor that is needed to determine the failure is to determine the actual stress in the vessel wall. The following relationships describe the membrane stress condition (Eq. 14), which is awakened by internal pressure in a vessel:

$$\sigma_t = \frac{pd}{2s}, \quad \sigma_a = \frac{pd}{4s}, \quad \sigma_r = -p$$  \hspace{1cm} (14)

From these tensions, the Huber-Mises-Hencky’s reduced stress can be determined (Eq. 15) at all temperatures:

$$\sigma_{\text{red}}^{\text{HMH}} = \frac{1}{\sqrt{2}} \left[ (\sigma_t - \sigma_a)^2 + (\sigma_a - \sigma_r)^2 + (\sigma_r - \sigma_t)^2 \right]$$  \hspace{1cm} (15)

2.5.1 Results of the stress calculations

Figure 9 shows the failure time of the structure. The stress in the vessel wall increases due to increasing pressure, according to the orange curve. The blue curve describes the change of the steel yield curve due to the wall heating. Disruption occurs when the two curves break apart; this value is at 425 seconds.

![Figure 9. Damage of the test vessel.](image)

2.6 Increase the failure time with greater wall thickness

One way the pressure vessel can carry out its task under extreme conditions if we increase its wall thickness. Calculations are made for vessels with the same parameters, but for three different wall thicknesses, and the evolution of failure time is shown in Figure 10.

![Figure 10. Destruction times of vessels with different wall thicknesses.](image)
By increasing the weight of the vessel, the vessel material itself is heated more slowly, so the steel yield curve varies with time. For wall thicknesses of 10 mm 425 sec., for wall thickness of 16 mm 720 sec. and for wall thickness of 22 mm, 965 seconds is the failure time. It is visible that a significant increase in destruction time can only be achieved with extreme wall thickness, but this causes unrealistic growth in mass and costs. Increasing the fire protection time by using this method is by no means economical.

2.7 Increase failure time with higher strength steel

Another method to increase the failure time is to increase the yield stress of the vessel material using better steel grade. In this case, the stress in the vessel wall will not change at the same wall thickness (10 mm) will cause the vessel to warm up at the same rate and as a result, the pressure increase will be the same. In this case, we determine a failure time of a nominal yield P235 MPa, P355 MPa and P460 MPa, as shown in Figure 11. In this case, the failure time of the pressure vessel for 355 MPa steel increased from 420 sec. (P235) to 650 seconds and for the 460 MPa steel it was 720 seconds in the fire. So, with this solution, we cannot increase the failure time significantly either. When using steel with an almost double yield stress, the damage will occur only 1.67 times later.

2.8 Increase failure time using fire protection coating

Longer failure time can also be achieved with fire protection coatings. One such solution is the use of scattered coatings. In this example, the vermiculite coating has been used. Vermiculite is a natural mineral (Al-Fe-Mg-silicate), which has a unique feature that it has a small plate structure, with crystalline water within the plates. By using the appropriate technology, the water between the fine layers is gassed, and the plates disintegrate. There is air between the expanded particles, which provides excellent thermal insulation.

The thermal conductivity of vermiculite coatings is between 0.1040-0.1530 W/mK and fire protection from 30 minutes up to 4 hours is available. The advantage of applying the coating to the surface that it does not require any postmanship; it is a relatively inexpensive solution and the disadvantage that it is not aesthetic [10, 11]. If a 15 mm thick vermiculite layer is placed on the vessel surface with a thermal conductivity factor of 0.12 W/mK then the failure time is shown in Figure 12. It can be seen that in this case this time will increase up to 2035 seconds, so that the vessel will hold for more than 30 minutes in the fire.

Figure 11. The failure times for various types of steel-grades.
3 Evaluation of results, additional objectives

In the case of pressure vessels, defining failure times due to fire is a much more complex task, than without fire and influenced by many factors:

- the size and geometry of the vessel,
- what type of fire and how far it acts,
- the material of the bowl,
- quantity and quality of the charge,
- fire protection solutions.

In our case, the failure of the test vessel was at 425 seconds after the fire occurred. At this time, the steel yield stress drops from 235 MPa to 162, and then the same value is reached by the stress rising in the vessel wall due to the increasing pressure. This time, therefore, can be very small, as it is not always possible to instantly detect the fire, and firefighters may need to have more time to arrive. It is therefore necessary to increase the fire resistance of the vessel for at least up to half an hour. There are several ways to do this: use a fire protection coating, increase wall thickness, use higher yield steel or design a built-in cooling system.

Three of these solutions were investigated, using higher wall thickness, higher yield strength and fire protection coatings. The results of these calculations are summarized in Table 1, which shows that the fire resistance time of 30 minutes can only be achieved with the coating under reasonable conditions. The second-best failure time, 16.08 minutes, was achieved by increasing the wall thickness of P235 steel.

The wall thickness of the container was 22 mm in this case, which is more than twice the size of the original; this solution is by no means economical. Increasing the steel yield stress has a benefit for the failure time, but not proportional to the cost [12]. The optimization of the supporting steel frame has also been made in the same way [13]. The fire protection coating has the best effect. The intumescent painting or the vermiculite coating can be applied [14-17].

The vermiculite coating has the best cost/protection ratio. Our other objectives include verifying the correctness of the model. We want to do this with measurements and some finite element modelling. This topic provides inexhaustible opportunities for both refining and testing. Recently we have made fire test and it strengthens our results, that after a relatively short period of time in the fire, the temperature of the pressure vessel was higher, more than 400 °C (Figure 13).
4 Summary

In the introduction of the paper, a short summary has been made about the possible causes and effects of chemical industry incidents, about the dangers of hydrocarbons, and the importance of conscious design and fire protection. The goal of the second part of the paper was to describe the vessel behaviour in case of fire.

First, we specified the changes in pressure and temperature, which are caused by an industrial fire. In this section two fire curves were also presented. For second step the changed strength parameters (yield stress of the steel is decreasing and the nascent stress in the vessel wall is increasing) caused by changing the physical properties, were specified. There are methods to increase the failure time of a vessel. In this case three methods have been discussed.

The increase of vessel’s wall thickness increase of steel grade and the application of fire-resistant coating. The one and only good solution was the usage of fire protection coating. This method fulfilled the criteria that the vessel reaches half an hour in a fire without rupture. Further investigation is needed to establish a model where safety valves are working and there are changes in the material volume inside the pressure vessel.
Acknowledgments
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5 Symbols

\( A_{\text{int}} \) the inside surface of the container \( m^2 \)
\( A_{\text{ext}} \) outer surface of the container \( m^2 \)
\( c \) thermal capacity \( J/(kgK) \)
\( f_y \) yield stress \( MPa \)
\( g \) gravitational acceleration \( 9,81 \frac{m}{s^2} \)
\( h_{\text{liq}} \) liquid level \( m \)
\( k \) heat conduction factor \( W/(mK) \)
\( k_{y,T} \) reduction factor -
\( L \) vessel height \( m \)
\( m \) mass of stored material \( kg \)
\( M \) molar mass \( g/mol \)
\( p \) pressure \( Pa \)
\( q_L, q_V, q_{LV} \) heat flow \( W \)
\( r \) vaporization \( J/kg \)
\( R \) universal gas constant \( 8,314413 \ J/(molK) \)
\( R_t \) vessel radius \( m \)
\( s \) vessel thickness \( m \)
\( t \) time \( s \)
\( T \) temperature \( K \)
\( V_L, V_V \) volume \( m^3 \)
\( Z_L, Z_V \) the height of liquid or gas in contact with heated wall \( m \)
\( \alpha_L, \alpha_V, \alpha_F \) heat transfer factor \( W/(m^2K) \)
\( \beta \) volume coefficient of thermal expansion \( 1/K \)
\( \varepsilon_L, \varepsilon_s, \varepsilon_f \) emissivity -
\( \Phi \) configuration factor \( I \)
\( \mu_L, \mu_V \) dynamic viscosity \( Pa.s \)
\( \rho_L, \rho_V, \rho_s \) density \( kg/m^3 \)
\( \sigma \) Stephan-Boltzmann constant \( 5,6703 \times 10^{-8} \ W/(m^2K^4) \)
\( \sigma_t \) surface tension of the liquid and between the steam \( N/m \)
\( \theta \) temperature \( ^\circ C \)

Indices

\( a \) the environment
\( ext \) external side
\( F \) flame
\( int \) internal side
\( L \) liquid
\( P \) propane
\( S \) steel
\( T \) vessel
\( V \) steam
The physical properties of propane in the function of pressure and temperature [13]

Liquid density ($\rho_L$)  

\[ \rho_L = -24,063 + 4,9636T - 0,0109T^2 \]

Steam density ($\rho_V$) from the general gas rule

\[ \rho_V = \frac{\rho_L}{T_0} \]

Liquid thermal capacity ($C_L$)

\[ C_L = 36309 - 230,2T + 0,39417T^2 \]

Steam thermal capacity ($C_V$)

\[ C_V = 168,03 + 5,6056T - 0,0014T^2 \]

Liquid thermal conductivity ($k_L$)

\[ k_L = 0,26755 - 6,6 \times 10^{-4}T + 2,77 \times 10^{-7}T^2 \]

Steam thermal conductivity ($k_V$)

\[ k_V = -0,0088 + 6 \times 10^{-5}T + 10^{-7}T^2 \]

Liquid dynamic viscosity ($\mu_L$)

\[ \mu_L = 709137T^{-3.986} \]
Steam dynamic viscosity (\(\mu_v\))
\[ \mu_v = 4.9054 \times 10^{-8} T^{0.90125} \]

Heat of vaporization (\(r\))
\[ r = 403.262 + 0.0682P \]

Molar mass (\(M\))
\[ M = 44.1 \]

Critical temperature (\(T_c\))
\[ T_c = 369.9 \]

Critical pressure (\(P_c\))
\[ P_c = 42.1 \]

Appendix 2 The constants of the Antoine equation for propane [14]

\[ \log_{10}(p) = A - \frac{B}{T + C} \]

where:

\[ \begin{align*}
A &= 4.53678 \\
B &= 1149.36 \\
C &= 24.906 \\
\end{align*} \]

\((p \text{ in bar}, T \text{ in } ^\circ\text{K})\)

---

*Figure A1. The relation between the pressure and the temperature of the propane.*