Physical-and-chemical calculations of safe mode of propane transportation

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Abstract: The key criteria used to assess fire-and-explosive hazard of any facility are: flash point, self-ignition temperature and minimum ignition energy. This article addresses how fire-and-explosive hazard criteria can be used to forecast emergency situations while transporting great quantities of flammable substance – propane, based upon ambient environment temperature. Calculations that were made have led to a conclusion that fire-and-explosive safety concentration mode for propane handling will be: lower concentration value is equal to 1.27 % or under than that value; upper concentration value is equal to 13.96 % or greater than that value. When selecting safe transportation and storage conditions for self-igniting combustible substances, great attention is given to relationship between environment, mass of substance transported and time-period to spontaneous ignition. For propane, the safe self-ignition temperature is deemed to be less than 360°C. Calculations for theoretical experiment regarding propane transportation were made based upon three critical temperature values: 1) 25 °C+10 °C - initial starting point when ambient temperature is 25 °C (roadway temperature is disregarded because ambient temperature is not high enough); 2) 60 °C+10 °C – point of arrival where ambient temperature is 60 °C; 3) 470 °C – propane self-ignition temperature. This helped us to figure out that propane can be stored and transported safely if the minimal electric ignition source is under $4 \times 10^{-6}$ Joule.

1. Introduction

Fire is a combustion capable of spreading on its own over long distances and supported by various types of combustion [1; 3]. Explosion is a rapid process of physical and chemical transformations of substances accompanied by release of significant amounts of energy within limited space which causes shock wave to be formed and spread in ambient space that can lead to occurrence of technological emergency [2; 4]. A fire-and-explosive hazard facility is a facility in which quickly-flammable and fire-explosive hazardous substances are produced, utilized, processed, stored or transported, thus creating a real threat of techno-genic emergency to occur. The key fire-and explosive hazard criteria associated with them are: flash point, self-ignition temperature and minimum ignition energy [5].
This theoretical research provides examples of how to calculate safe modes of handling combustible substance – propane.

Propane is a colorless gas. Nowadays it has a wide range of applications in industry, domestic use and automobile transport. Its formula is \( C_3H_8 \) [6]. In domestic use though, propane is most often referred to as a mixture of butane and propane. Low quantities of other gases may be admixed to it as well. The fact that pure propane is odorless makes it quite dangerous because of the difficulty to identify and prevent gas leakage, so this can cause an aftermath [7]. That is the reason why propane mix composition often includes a substance having a pungent odor - an odorant. Propane mix is transported in pressurized steel vessels with 16 atm. pressure maintained [8].

The purpose of these calculations is to ensure that large quantities of propane (over 800 liters) can be transported in a safe manner from point A (ambient temperature +25 °C) to point B (ambient temperature + 60 °C). During this process, vehicle will have to be able to make stops as required.

2. Methods

The following will be analyzed:

- Detailed review of properties of combustible substance (air reaction equation; whether or not the substance burns; CLFPs - concentration limits of flame propagation).
- Conditions for thermal spontaneous combustion.
- Minimum ignition energy of this substance.
- At what minimum electrical energy would propane be safe for other substances that are less flammable [9].

3. Results and discussion

Equation of reaction by air

\[
C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 5 \times 3.76N_2 + Q,
\]

where \( \beta \) - is the coefficient in the chemical reaction placed before oxygen (\( \beta = 5 \)) that shows how much oxygen is needed for complete combustion of 1 mole of a combustible substance.

Combustibility factor (1):

\[
Kr = 4^* (C)_n + 4^* (S)_n + (H)_n - 2(O)_n - 3(F)_n - 2(Cl)_n - 5(Br)_n
\]

let's substitute the values:

\[
Kr = 4^* 3 + 8 = 20
\]

Combustibility coefficient is greater than one, which means that propane burns well.

Concentration limits of flame propagation are calculated by formula (2):

\[
\varphi_{L(H)} = \frac{100}{\alpha \times \beta + b} \%
\]

where \( \alpha \) and \( b \) - are coefficients provided in table 1; \( \beta \) - is the coefficient placed before oxygen in the chemical reaction.

| CLFPs | \( A \) | \( B \) |
|-------|--------|--------|
| LCLFP | 8.684  | 4.679  |
| HCLFP \( \beta \leq 7.5 \) | 1.550  | 0.560  |
| HCLFP \( \beta > 7.5 \) | 0.768  | 6.554  |
The lowest concentration limit of flame propagation (LCLFP) is calculated by formula (3):

\[
\phi_{L,H} = \phi_L \left(1 - \frac{T - T_0}{1550 - T_0}\right), \% \tag{3}
\]

*Note: Instead of 1150, let’s assume the temperature value to be equal to 1550 – this is because we need to foresee the most dangerous modes of handling the substance.

The highest concentration limit of flame propagation (HCLF) is calculated by formula (4):

\[
\phi_{H} = \phi_L \left(1 + \frac{T - T_0}{1100 - T_0}\right), \% \tag{4}
\]

In order to calculate the LCLFP and HCLFP, we need to know the initial temperature and changed temperature. Therefore, \(T_0\) will be equal to +25 °C; \(T\) will be assumed equal to 80 °C which is based upon the sum of the following recorded temperatures: 60 °C - ambient temperature; 10 °C – temperature generated by road surface; 10 °C – temperature generated by vehicles’ working engine (assuming that the vehicle that transports propane has no cooling system in the back). To obtain more accurate calculated temperature values, Kelvin scale will be utilized instead of Celsius scale. Therefore, the calculations are:

\[
\phi_L = \frac{100}{8.684 \times 5 + 4.679} = 2.08\% \\
\phi_{L,H} = 2.08 \times \left(1 - \frac{(273 + 80) - (273 + 25)}{1550 - (273 + 25)}\right) = 1.99\% \\
\phi_H = \frac{100}{1.550 \times 5 + 0.560} = 12.03\% \\
\phi_{H} = 12.03 \times \left(1 + \frac{(273 + 80) - (273 + 25)}{1100 - (273 + 25)}\right) = 12.85\%
\]

HCLFP (12.85%) is the gas concentration threshold in the vapor-air mix, equal to a given value and less than it, at which propane will ignite spontaneously under given conditions (regardless the distance to the ignition source).

LCLFP (1.99%) is the gas concentration threshold in the vapor-air mix, equal to and greater than this value, at which propane will ignite spontaneously under given conditions.

Please note that no ignition will occur below LCLFP; but if there is an ignition source, then 1.5% of LCLFP content will be sufficient to cause the substance to self-ignite. Therefore, propane is in its safest condition when its concentration is under 1% in vapor-air mix under given conditions.

In order to reduce fire-and-explosion hazard of substances, i.e, to achieve safer modes of operation, phlegmatizer is utilized – it can be liquid, solid or gaseous substance admixed to combustible substance to reduce its sensitivity to environmental factors.

Therefore, phlegmatizer can possibly be used to reduce the size of affected areas. At the same time one needs to know that phlegmatizer can not eliminate affected area, it can only reduce its size through reduction of HCLFP.

Using CLFP values, safe propane concentrations are calculated using formulas (5) (6):

\[
\phi_{saf(L)} \leq 0.9 \times (\phi_L - 0.7 \times R)\% \tag{5}
\]

\[
\phi_{saf(L)} \leq 0.9 \times (2.08 - 0.7 \times 0.95) = 1.27\%
\]
\[ \phi_{\text{safe}(H)} \geq 1.1 \ast (\phi_H + 0.7 \ast R) \% \]  
\[ \phi_{\text{safe}(H)} \geq 1.1 \ast (12.03 + 0.7 \ast 0.95) = 13.96 \% \]

4. Conclusion

Fire-and-explosion-safe propane concentrations will be at the lowest value \( \phi_{\text{safe}} \leq 1.27 \% \), i.e. safe concentration equal to 1.27% or less than this value; at the upper value of \( \phi_{\text{safe}} \geq 13.96 \% \), i.e. the safe concentration is 13.96% or above.

Let us review the thermal spontaneous ignition conditions. These conditions apply when selecting safe conditions for processing, transportation and storage of flammable combustible substances. A substance is considered to be safe at a temperature equal to:

\[ t_{\text{safe}} < 0.8 \ast t_{\text{env}} , \]

where \( t_{\text{env}} \) - is the minimum temperature of environment at which substance’ self-ignition occurs.

Both in the Russian Federation and abroad, there are legal regulations in force that establish unified parameter values for various substances. Therefore, self-ignition temperature values for many substances are known and can be found in reference literature.

\( t_{\text{env}} \) (propane) = 470°C.

\( t_{\text{safe}} < 0.8 \ast 470 = 360°C \), therefore, safe temperature for propane will be any temperature below 360 °C.

Let us investigate the minimum ignition energy. When calculating this parameter, we should, in most cases, add 10 °C to ambient temperature values because propane is transported by vehicles (trucks), and each truck has certainly got a running engine that emits heat; we should also add 10 °C because this is the amount of heat that comes up from the roadway.

Calculations will be made at the following temperatures: 1) 25 °C + 10 °C - the original starting point where the ambient temperature is 25 °C (road temperature will be disregarded because the ambient temperature is not high); 2) 60 °C +10 °C +10 °C - point of arrival, where the ambient temperature is 60 °C; 3) 470 °C – propane self-ignition temperature.

These calculations will be made by using formula (7) (8):

\[ W_i = \alpha \ast q \ast l_{\text{critical gap}} \ast \text{Joule} \]  
\[ q = \int_{t_{\text{start}}}^{t_{\text{arrival}}} Cp \ast \rho_i \ast dt. \]  
\[ t_{\text{start}} = 25 + 10 = 35°C \quad \text{and} \quad t_{\text{arrival}} = 60 + 10 + 10 = 80°C; \quad t_{\text{self-ignition}} = 470°C; \quad dt \quad \text{temperature variance. Based upon table 2:} \]

| \( t, °C \) | Air heat capacity, kJoule, \( C_p \) | Heat used to heat-up 1 m³ of air, kJoule, \( \rho_j \) |
|---|---|---|
| 35 | 1.152 | 17 |
| 80 | 1.099 | 66.2 |
| 470 | 0.560 | 294.3 |

At propane’s self-ignition temperature of 470°C:
\[ q = (0.560 \times 294.3) \times 10^6 = 1.648 \times 10^8 \]

\[ W_{470} = 0.5 \times 1.648 \times 10^8 \times (0.25 \times 10^{-3})^3 = 0.824 \times 10^8 \times 0.015625 \times 10^{-9} = 0.01287 \times 10^{-1} = 1.287 \times 10^{-3} \text{Joule} \]

At the initial temperature of 35°C:

\[ q = (1.152 \times 17) \times 10^6 = 1.958 \times 10^7 \]

\[ W_{\text{ignition}}(35) = 0.5 \times 1.958 \times 10^7 \times (0.25 \times 10^{-3})^3 = 1.32 \times 10^7 \times 0.015625 \times 10^{-9} = 0.01 \times 10^{-3} \text{Joule} \]

At the initial temperature of 80°C:

\[ q = (1.099 \times 66.2) \times 10^6 = 7.275 \times 10^5 \]

\[ W_{\text{ignition}}(80) = 0.5 \times 7.275 \times 10^5 \times (0.25 \times 10^{-3})^3 = 36.3 \times 10^5 \times 0.015625 \times 10^{-9} = 0.56 \times 10^{-3} \text{Joule} \]

Based upon these calculations, propane will ignite if the ignition source has a minimal energy of \( W_{\text{ignition}}(35^\circ \text{C}) \) that equals to \( 0.01 \times 10^{-3} \text{Joule} \). In this case, propane itself would become an ignition source for less flammable substances. Any violation of flammable substances handling procedures can result in fire hazard situation.

As for the safe minimum energy for ignition, for propane it would be the value calculated by formula (9):

\[ W_{\text{safe}} < 0.4 \times W_{\text{min}}, \text{Joule} \quad (9) \]

Let us substitute: \( 0.4 \times 0.01 \times 10^{-3} = 4 \times 10^{-6} \text{Joule} \).

Therefore, propane can be stored and transported if the electric ignition source is not above \( 4 \times 10^{-6} \text{Joule} \).

5. Summary

The fire-and-explosion-safe concentration mode for propane handling will be: lower concentration value is 1.27% or less than this value; upper concentration value is 13.96% or greater than this value.

When selecting safe conditions for processing, transportation and storage of self-igniting combustible substances, much attention is given to relationship between the environment, the mass of substance and time to spontaneous ignition. For propane, the safe self-ignition temperature is considered to be any temperature under 360°C.

Propane can be stored and transported if the electrical ignition source does not exceed \( 4 \times 10^{-6} \text{Joule} \).

6. Recommendations

- Prior to transporting any combustible substance, make sure calculations have been made that include environmental factors (relative humidity, roadway temperature, engine-emitted temperature, temperature fluctuations).
- Transport propane in concentrations of less than 1%.
- Make sure phlegmatizer is used.
- Follow flammable cargo transportation procedures with cooling systems utilized.
- When transporting propane, never make stops in locations where large quantities of other combustibles can be potentially present or actually present because they can be a source of ignition for propane and vice versa.
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