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Simplified Model of the Internal Atmosphere of Flammable Liquid Tanks in Case of Air Inlet from a Pressure Safety Valve

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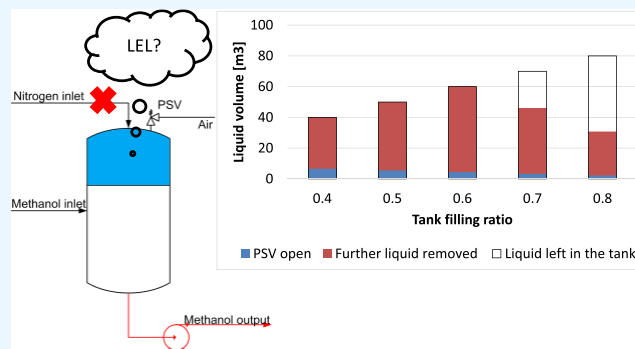
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ABSTRACT: Storage of flammable liquids is a common activity in many industrial domains. A history of accidents shows that liquid storage has been involved in several critical accidents due to the large amount of hazardous substances potentially involved in the incident. Safe storage of flammable liquids is often guaranteed through blanketing of the internal atmosphere of the tank through the introduction of an inert gas, usually nitrogen. A double action pressure safety valve is often installed on the tank to protect the tank from damage in the event of overpressure or depression. In case of depression, an inert gas, usually nitrogen, is fed to the vapor space of the tank to maintain the vapor composition outside of the flammability limits. In case of lack of nitrogen, the opening of the pressure safety valve allows air to enter. The entry of air, especially if prolonged, can bring the atmosphere inside the tank to explosive conditions. This paper presents a simplified model for the estimation of the internal composition of the tank following the entry of air due to the opening of the pressure safety valve, following the process of fluid removal in case of lack of nitrogen. The model also allows the estimation of how much liquid can be safely removed. The simplified model can analyze both the case of a single tank and a tank farm.



INTRODUCTION

Storage of flammable liquids is a common activity in many industrial domains. Depending on operational or safety constraints, tanks are often included in dedicated areas, known as tank farms. Accident records allow recognizing tank farms as particularly risky areas due to the large amounts of hazardous substances stored,^{1,2} even though they are not usually handled under dangerous conditions, e.g., high temperatures or high pressures. At the same time, tank farms are guarded by a less number of personnel and consequently have a low probability of a rapid identification of possible faults. The number of accidents occurring in storage is not negligible; in fact, Chang et al.³ listed more than 240 accidents in the past 40 years. Zheng and Chen⁴ noted that in the last 50 years, over 60% of the accidents in the Chinese petrochemical industry involved storage or process tanks. Accidents in tank farms can cause major consequences in environmental, safety, or economic terms.^{5,6}

Whenever possible, the safety of the storage tanks relies on keeping the saturation conditions in the vapor space of the tanks. Otherwise, as in the case of saturation conditions that fall between the flammability limits (e.g., for methanol), the safe management of tanks requires the adoption of blanketing with inert gas, usually nitrogen or carbon dioxide, implemented with the other measures able to minimize ignition sources, such as grounding.⁷

In blanketing, the atmosphere inside the tank is made inert by replacing the internal air with an inert gas, such as nitrogen. Although it is an industrially widely used technique, in the literature, it is poorly treated.^{8,9} For example, Capón-García et al.¹⁰ report a methodology to optimize blanketing activities in tank farms.

The most used blanketing method¹¹ consists of inserting inert gas when the pressure drops and venting the internal atmosphere when the pressure rises. The pressure can have variations due to operations and temperature, and in case of pressure control errors, due to overpressure or depression, tank damage can occur. Thus, the tanks are equipped with vent valves. In the event of depression due to insufficient inert gas entry, a two-way vent valve (pressure safety valve, PSV) allows air to enter. If prolonged, the entry of air can make the internal atmosphere flammable.

In the event of transient problems in the supply of inert gas, to ensure the continuity of operation of the plant, it is

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necessary to know the composition inside the tank to avoid the formation of dangerous atmospheres. In this paper, a simplified model for assessing the internal composition of the tank is proposed.

The model is initially detailed for a single tank, but since often flammable liquids are stored in multiple tanks, the model is extended for this further case. In these cases, the internal pressure of the tanks is kept the same in the different tanks through an equilibrium tube. The equilibrium tube is a pipe that connects the atmosphere of the different tanks. The simplified model is thus adapted to the case of tank farms where tanks are connected by an equilibrium tube. Also in this case, the simplified model helps understanding if during the emptying of the tanks, in the event of the absence of inert gas flow, the atmosphere of at least one tank becomes flammable.

The simplified models proposed here are intended for the identification of the safe conditions enveloped within a plant, from an operational point of view, but also as a support for the risk-based decision making, integrating the simulation results within risk assessment.

Several efforts have been made in recent years to integrate logical and probabilistic analysis with the phenomenological one to obtain a risk assessment more representative of the specific process, such as initially in Bosca et al.,¹² applied to the freeze-drying process, then in Demichela and Baldissone¹³ and Baldissone et al.,¹⁴ where the concept was applied to an intensified process for the treatment of VOCs and organizational environments, and in Baldissone et al.¹⁵ and Demichela et al.,¹⁶ related to the optimization of critical procedures.

This paper represents a step forward in this direction, built on the preliminary work of Baldissone et al.¹⁷

MATERIALS AND METHOD

The model described below allows estimating the composition of the atmosphere inside an inerted tank containing a

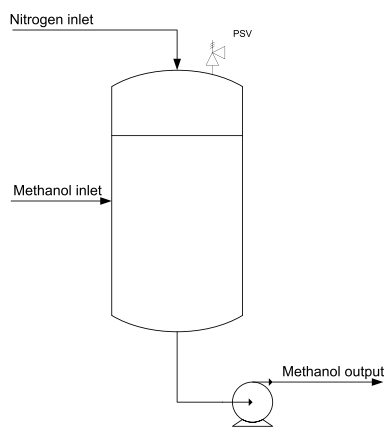


Figure 1. Simplified scheme of a single storage tank, with a blanketing system.

flammable liquid after the inlet of air following the opening of the PSV. In a second step, it is possible to estimate how much liquid can be removed before the atmosphere of the tank becomes flammable.

In a second step, the case of tank farms is modeled. In this case, a tank farm is modeled considering the tanks joined through an equilibrium tube. In this way, when the inert gas flow is stopped, the tank farm should be considered. However, from a phenomenological point of view, the opening of the

PSV will affect only the composition of the atmosphere of the tank whose PSV is intervened, as it is assumed that the entry of air is initially limited to this tank. The model estimates how much additional liquid can be removed before the atmosphere inside the tank becomes flammable in the absence of nitrogen flow.

For both models, it is assumed that an isothermal behavior is present and, as a starting condition, that the vapor phase inside the tank is in equilibrium with its liquid.

Single Tank. In this part, the model for a single tank is described; the tank scheme is shown in Figure 1. The simplified model considers three phases:

1. Initial pressure decrease.
2. PSV opening and pressure balancing.
3. Further removal of liquid.

Initial Pressure Decrease. The inert gas flow is absent, and liquid is removed from the tank with a decrease in pressure. Under these conditions, the pressure drops. The mass balance (eq 1) describes how the volume occupied by the gas varies during the removal of the liquid.

$$\frac{dV_g}{dt} = L \quad (1)$$

where V_g is the volume of the tank occupied by the gas phase. L is the volume flow rate of liquid removed from the tank.

Considering the equation of ideal gases, it is possible to derive the trend of the pressure (eq 2).

$$\frac{d}{dt}(P \cdot V_g) = 0 \quad (2)$$

where P is the internal pressure of the tank.

In this phase, the composition of the atmosphere is considered constant at equilibrium conditions, until the opening of the safety valve.

PSV Opening. The opening the PSV is modeled with the consequent entry of air until the pressure is restabilized. This phase is considered short, so the evaporation of the liquid can be neglected.

By applying the mass balance and the equation of perfect gases (eq 3), the amount of air needed to restore the internal pressure can be obtained.

$$\begin{cases} V_g \cdot \frac{dP}{dt} = R \cdot T \cdot \frac{dN}{dt} \\ \frac{dN}{dt} = N_a \end{cases} \quad (3)$$

where N is the quantity of material in the gas phase, R is the constant of the ideal gas, T the temperature, and N_a is the air entering the tank.

To obtain the composition inside the tank, the mass balance of the single component (eq 4) is used; the perfect mixing is assumed.

$$\begin{cases} \frac{d}{dt}(N \cdot y_{N_2}) = 0 \\ \frac{d}{dt}(N \cdot y_a) = N_a \\ y_v + y_{N_2} + y_a = 1 \end{cases} \quad (4)$$

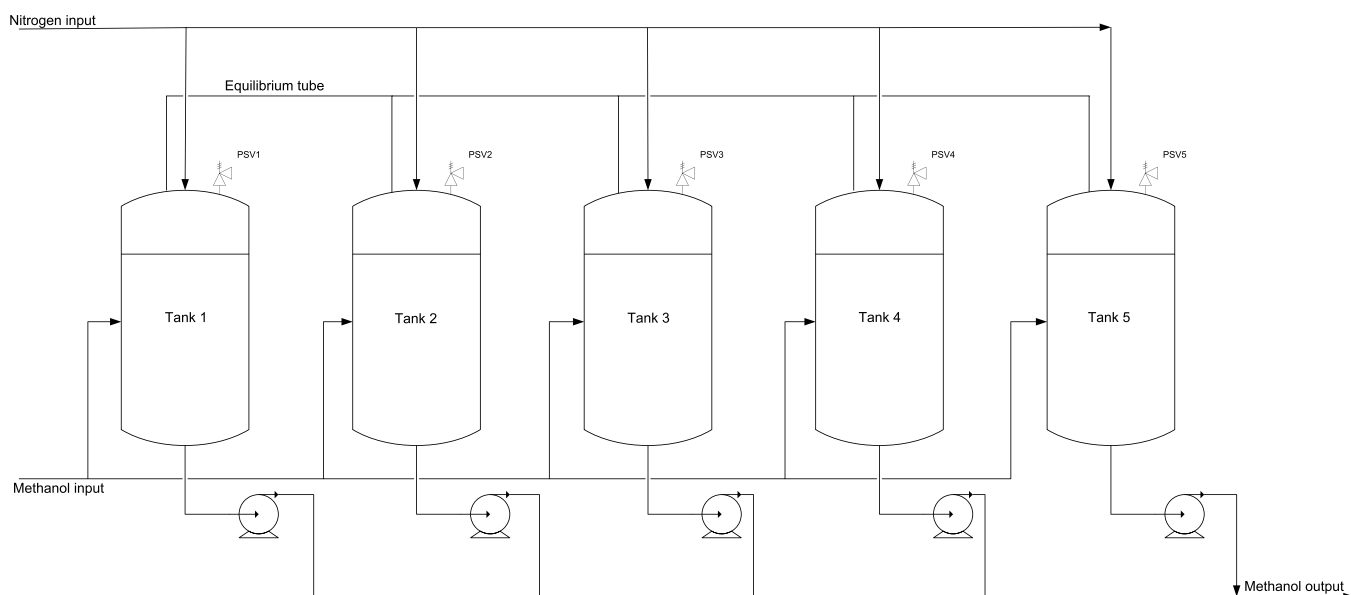


Figure 2. Simplified scheme of a tank farm with a blanketing system.

where y_{N_2} is the fraction in moles of nitrogen, y_a is the fraction of air, and y_v is the fraction of vapors.

The composition of the atmosphere is then compared with the limits obtained in accordance with Ma,¹⁸ who developed a procedure to estimate the flammability limits of a mixture.

Further Liquid Removal. When the liquid is further removed from the tank, the pressure continues to be balanced through the entrance of air via the PSV. Modeling stops when the tank is emptied or when the flammability conditions are reached. In this way it is possible to assess the maximum quantity of removable liquid, while maintaining safety conditions.

In this phase, through the mass balance and the equation of ideal gases, the flow rate of the incoming gases (N_{IN}) can be obtained (eq 5):

$$\begin{cases} \frac{dV_g}{dt} = L \\ P \cdot \frac{dV_g}{dt} = R \cdot T \cdot \frac{dN}{dt} \\ \frac{dN}{dt} = N_{IN} \end{cases} \quad (5)$$

If a rapid removal of liquid is assumed, the incoming gas consists only of air as the quantity of vapors is negligible (eq 6):

$$\begin{cases} N_a = N_{IN} \\ N_v = 0 \end{cases} \quad (6)$$

Instead, when the removal of liquid is slow, the incoming gas is saturated with vapors, and eq 7 can be used:

$$\begin{cases} N_a = N_{IN} \cdot (1 - y_{sat}) \\ N_v = N_{IN} \cdot y_{sat} \end{cases} \quad (7)$$

where y_{sat} is the saturation fraction of the vapor and N_v is the quantity of the vapor product.

The results of the model will be given for both the cases, obtaining a range of possible outcomes.

The composition of the vapor phase can be obtained through the mass balance of the single component, (eq 8):

$$\begin{cases} \frac{d}{dt}(N \cdot y_{N_2}) = 0 \\ \frac{d}{dt}(N \cdot y_a) = N_a \\ \frac{d}{dt}(N \cdot y_v) = N_v \end{cases} \quad (8)$$

In this way, the maximum amount of removable liquid before the vapor phase enters the flammability conditions or the tank is emptied can be evaluated.

Tank Farm. This section describes the model developed for a tank farm; the plant scheme is shown in Figure 2. This model is also divided into the three phases as described above.

Pressure Reduction. In this phase, the inert gas flow fails but the liquid continues to be removed, leading to a decrease in pressure. This phase ends when the PSV opening pressure is reached.

In this case, eqs 1 and 2 are still valid. However, since the tanks are connected through an equilibrium pipe, the volume of gas to be considered in the equations is the volume of gas contained in all the tanks' vapor space.

The composition of the atmosphere inside the tanks is assumed to be the equilibrium one.

PSV Opening. Air enters from the PSV, restoring the pressure. In case of rapid entrance, the evaporation of liquid is considered negligible. The quantity of the incoming air must re-establish the pressure in the entire tank farm connected through equilibrium tubes.

To estimate the composition, eq 4 is used.

Further Liquid Removal. In this case, it is assumed that the liquid is further removed from the tank whose PSV opened, while no liquid is removed from other tanks.

The air flow is estimated with eq 5.

The composition of the internal atmosphere is estimated with eqs 6 and 8 in case the liquid removal is rapid and the evaporation is negligible. Instead, eqs 7 and 8 are used in case the removal of the liquid is slow, so the incoming air is saturated with vapors.

RESULTS

Single Tank. The single tank model is applied to the case of a tank containing methanol and inerted with nitrogen. The tank has a volume of 100 m³.

Table 1. Atmosphere Composition after the PSV is Opened and the Pressure is Rebalanced

PSV opening depression (kPa)	methanol fraction	air fraction	nitrogen fraction
2.5	0.162	0.025	0.813
5	0.158	0.049	0.79
10	0.150	0.010	0.75
25	0.125	0.247	0.628

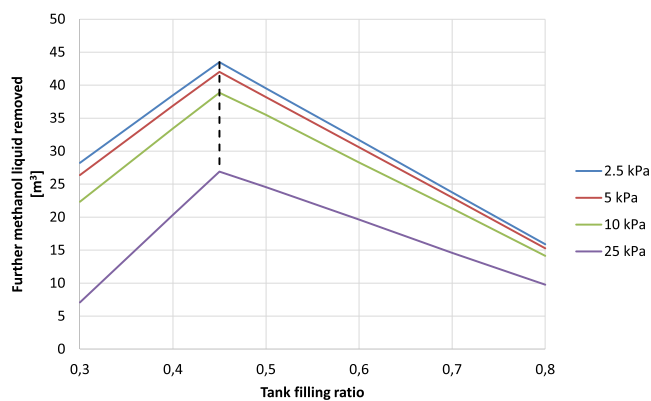


Figure 3. Methanol liquid volume removed before the tank atmosphere became flammable, in case of rapid liquid removal.

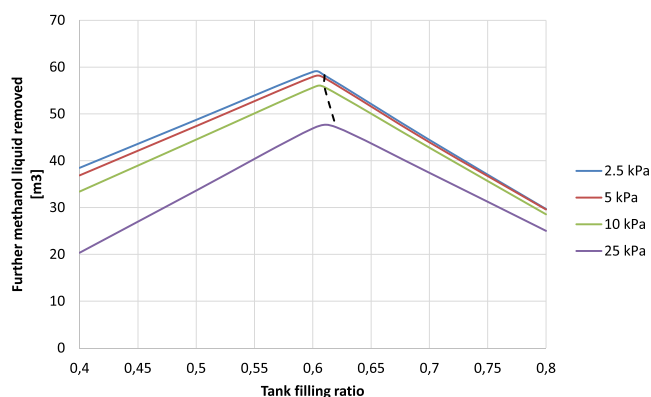


Figure 4. Methanol liquid volume removed before the tank atmosphere became flammable, in case of slow liquid removed.

The tank is equipped with a PSV. Different opening depression values of the PSV, 2.5, 5, 10, or 25 kPa are analyzed. Table 1 shows the composition of the internal atmosphere of the tank, 70% full of liquid, after the interruption of the nitrogen flow and the opening of PSV to rebalance the pressure:

Figures 3 and 4 show the maximum amount of liquid that can be safely removed; on the vertical axis, with respect to the

filling rate of the tank at the time of interruption of the nitrogen flow, and on the horizontal axis, in case of rapid liquid removal (Figure 3) and slow liquid removal (Figure 4).

In both figures, at the left of the dotted line, all the liquid contained in the tank can be safely removed.

Figure 3 shows that in case of a slow removal of liquid, a filling ratio lower than 45% allows the tank to be completely emptied maintaining the safe conditions, while with the rapid removal of liquid, represented in Figure 4, the initial filling ratio allowing the safe removal of the whole amount of liquid is lower than 60%.

The abovedescribed behaviors are made more explicit in Figure 5, where the amount of liquid removed before and after PSV opening compared with the available volume of liquid according to the filling ratio are represented, for the rapid (a) and slow (b) removal of liquid.

Figure 6 allows a direct comparison of the behavior at different PSV set points in case of rapid or slow liquid removal.

Tank Farm. The model is also applied to the case of a tank farm with five tanks of 100 m³ containing methanol and inerted with nitrogen. This paper reports the cases in which a PSV is installed with an opening depression of 2.5, 5, or 10 kPa. For the tank farm, the case of 25 kPa PSV set point has not been considered since in most of the simulations, the tank was emptied before the intervention of the PSV, so the case was not considered.

Figure 7 shows the compositions of the atmosphere inside the tank after the opening of the PSV. The concentrations of methanol and nitrogen are estimated and compared with the flammability diagram, for different filling ratios of the whole tank farm and of the tank whose PSV was opened.

At the PSV set point of 2.5 kPa, the atmosphere does not become flammable for any filling ratio. While for the higher set point, conditions can be found that bring the concentrations in the vapor space within flammable limits.

Figure 8 shows the maximum amount of liquid that can be safely removed from the tank whose PSV is opened, with different filling ratios of the tank farm, in case of rapid removal of liquid.

Figure 9 shows the analogous results in the case the liquid is slowly removed, so that the incoming gas is saturated with vapors.

In Figures 8 and 9, the lines that appear as interrupted represent two limit conditions:

- When interrupted on the left (at a low filling ratio), they represent situations in which the tank is emptied before the pressure reaches the PSV set point.
- When interrupted on the right (at a high filling ratio), they represent the case in which the vapor space is already under flammable condition.

In this case, the tank can be emptied if the filling is less than about 60%. Also, in this case, at the increase of the PSV opening set point, the quantity of liquid that can be safely removed decreases.

CONCLUSIONS

Storage in tanks is often regarded as low-risk activity as hazardous substances are not handled or manipulated. However, given the large quantities of substance potentially involved in an accident, the consequences can be very serious. Furthermore, in the past, the flammable liquid storage tanks have often been involved in accidents.

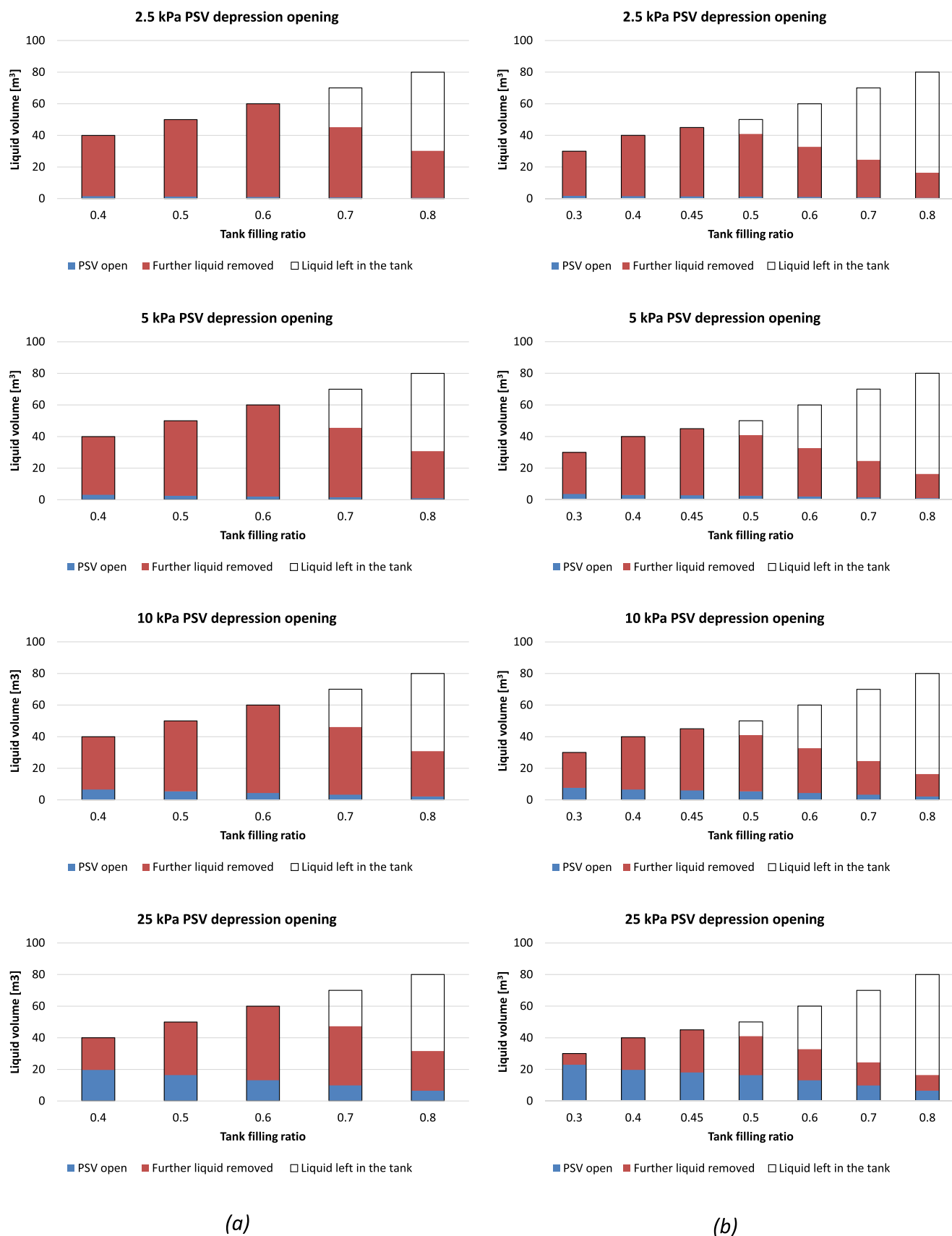


Figure 5. Methanol liquid volume removed before the tank atmosphere became flammable, for slow (a) and rapid (b) liquid removal at different PSV set points, compared to the liquid volume initially in the tank.

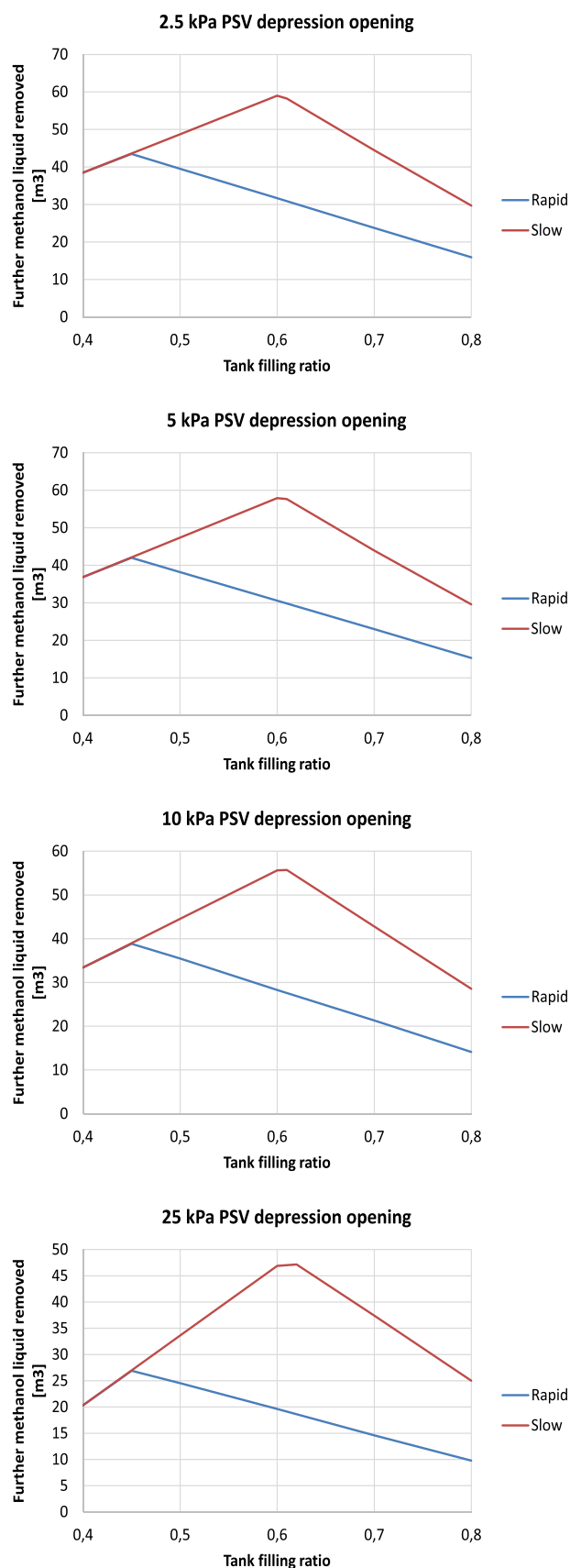


Figure 6. Methanol liquid volume removed before the tank atmosphere became flammable, comparison for rapid and slow liquid removal at different PSV set points.

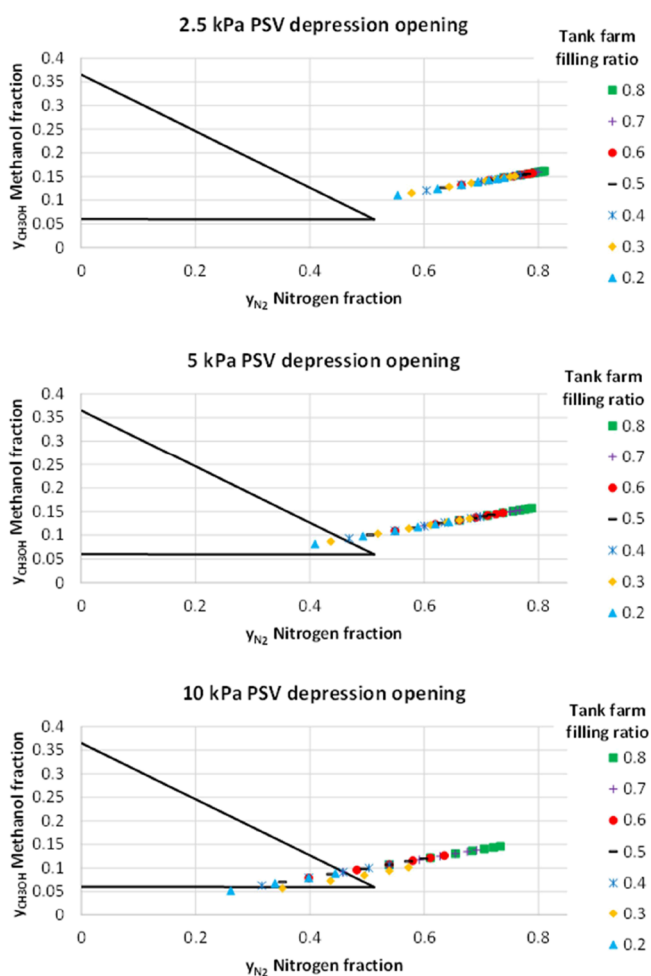


Figure 7. Composition in the vapor space after the opening of the PSV to air.

When flammable liquids are stored in tanks, blanketing is mostly used to keep them under safe conditions. In blanketing, the atmosphere inside the tank is made inert through the feed of an inert gas. The tanks are usually equipped with a PSV to prevent damage in the event of overpressure or depressions. In case of depression and lack of inert gas, the opening of the PSV allows the entry of air, which, if prolonged in time, can bring the internal atmosphere of the tank within flammability conditions.

While the main attention is paid to the case of release of material from the tank to the atmosphere, the case of the entrance of air in the tank, hopefully protected by the grounding system, is less considered.

This paper presents a simplified model to estimate the composition inside the tank following the opening of the PSV and the entry of air. With the simplified model, it is possible to estimate the maximum quantity of liquid that can be safely further removed, in the absence of inert gas flow.

This model is tested in the case study of a methanol tank. The quantity of liquid that can be safely removed from the tank depends on its filling ratio and the opening set point of the PSV.

When the tank is part of a tank farm, the simplified model can also be applied, by observing the composition of the atmosphere of the tank whose PSV opens.

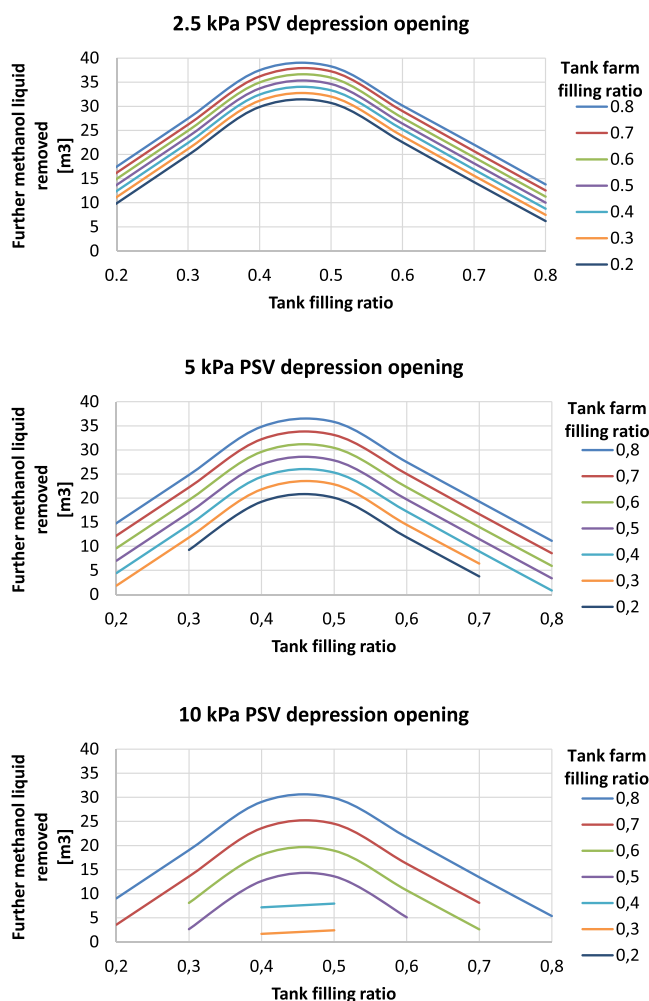


Figure 8. Methanol liquid volume removed before the tank atmosphere became flammable, in case of rapid liquid removal.

The simplified model developed is intended to be used by plant operators to define the safe envelop of their operations under nonstandard conditions.

This initial work is prodromic to the definition of a soft-sensor able to monitor with continuity the state of the tank vapor space, extending the adoption of advanced data analysis and exploitation techniques in the process industry risk assessment and management¹⁹ related to prognostic risk assessment,²⁰ related to maintenance strategies for process equipment or Demichela et al.,²¹ related to the prognostic and health management of aging equipment, and, more recently,²² related to the development of an innovative sensing system for environmental conditions, which could be exploited in the work environment real time monitoring.

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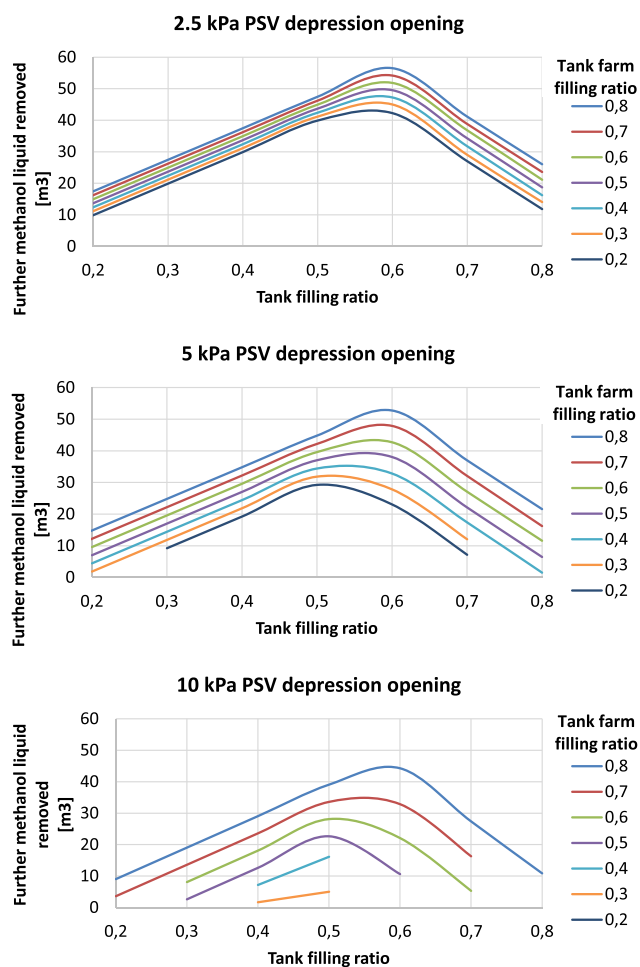


Figure 9. Methanol liquid volume removed before the tank atmosphere became flammable, in case of slow liquid removal.

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Notes

The authors declare no competing financial interest.

NOTATION

$V_{g'}$, m ³	Volume of the tank occupied by the gas phase
t , s	Time
L , m ³ /s	Volume flow rate of liquid removed from the tank
P , Pa	Internal pressure of the tank
R , m ³ ·Pa·K ⁻¹ ·kmol ⁻¹	Constant of the ideal gas
T , K	Temperature
N , kmol	Quantity of material in the gas phase
$N_{a'}$, kmol	Quantity of air entering in the tank
y_{N_2} , kmol/kmol	Mole fraction of nitrogen
y_v , kmol/kmol	Mole fraction of vapor
$y_{a'}$, kmol/kmol	Mole fraction of air
$N_{v'}$, kmol	Quantity of gas entering in the tank
$N_{v'}$, kmol	Quantity of vapor product
y_{sat} , kmol/kmol	Mole fraction of saturation vapor

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