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Preliminary Risk Evaluation of Methanol/Water Storage in Fuel Cell Integrated Systems for Onboard Applications

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In this work, a preliminary risk evaluation of the methanol/water storage in fuel cell integrated systems is performed. The system which couples methanol steam reforming and the fuel cell to generate electricity is considered as a solution in several industrial projects for onboard applications. The challenge of such a system is to control the thermal loads to operate under fully autothermal conditions, recycling the dissipated heat from the fuel cell to preheat and evaporate the reactant mixture. To implement these systems, safety issues must be identified and minimized. Considering the autothermal operating conditions of the methanol steam reforming unit, the water/methanol ratio was set at 3. Under these conditions, the mixture is safer than pure methanol in terms of flammability and toxicity, but not yet inherently safe. Starting from the generation of a hole on the storage tank as initiating event, the consequence analysis as well as some preliminary risk considerations is performed by using empirical models. In this work, the focus was on the effects of a vapour cloud explosion and comparisons were made between a methanol-water solution, pure methanol, and gasoline, used in the conventional internal combustion engine.

1. Introduction

The mobile sector, such as automotive and marine, plays a crucial role in the emissions of greenhouse gases. With the global shift towards the circular economy, one of the main strategies of the European Commission to reduce gas emissions is to speed up the deployment of low-emission alternative energy for transport, such as advanced fuels, biofuels, renewable synthetic fuels, hydrogen, and technologies alternative to conventional internal combustion engine (ICE) like as Fuel Cells (European commission, 2020). In this scenario, methanol is a promising fuel and hydrogen source for several advantages, such as the possible use as a pure liquid or in solution, the negligible sulphur content, high hydrogen/carbon ratio and the possible production from renewable resources and the low reforming temperature (Harmsen et al., 2020). Therefore, methanol can be considered an efficient hydrogen storage system that facilitates the introduction of proton exchange membrane fuel cell (PEMFC) technology, as the transport and storage infrastructure can be built more easily compared to gaseous or liquid hydrogen. The automotive sector, which accounts for about 20% of greenhouse gas emissions, has already recognized these benefits and is investing heavily in the development of vehicles based on methanol steam reforming for hydrogen production and PEMFC for energy generation. Recently, the Chinese start-up Aiways presented a sports car designed by German engineer Roland Gumpert at the Beijing Motor Show in April 2020, equipped with a PEMFC integrated into a methanol reformer (AIWAYS, 2020). In addition, the use of methanol-based infrastructures as an alternative to conventional maritime fuels is being developed in shipping technology, as was also proposed in Rina's Everywh2ere project, which won the 2021 Best Innovation Award (Gurau et al., 2020; RINA, 2023). The main units of the methanol technology coupled with the HT-PEMFC are the methanol/water storage tank, the steam reforming reactor, and the fuel cell. This configuration enables a significant improvement in energy efficiency and environmental protection compared to conventional ICE technology. The use of methanol as hydrogen source allows removing hydrogen storage under pressure on board, thus significantly reducing the associated risks. However, with a view to widespread diffusion of PEMFC technology based on methanol reforming, several aspects should be further investigated, most notably safety, which has generally received little attention in the literature despite its importance.

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Furthermore, one of the main challenges in the application of this integrated system is the correct control of the thermal loads to achieve an autothermal system. To this end, the best operating conditions in terms of water/methanol ratio, air/methanol ratio and reactor operating temperatures must be determined to energetically sustain the process by using the heat losses from the fuel cell. This heat must be used to preheat and evaporate the reactants. In this paper, we present the comparison between the gasoline-based and methanol-based technologies by performing a consequences analysis and a preliminary risk evaluation. The consequences analysis was carried out using appropriate empirical models. At this stage, the comparison was carried out by focusing the attention to the generation of a hole on the storage tank and the occurrence of a vapor cloud explosion.

2. Methodology

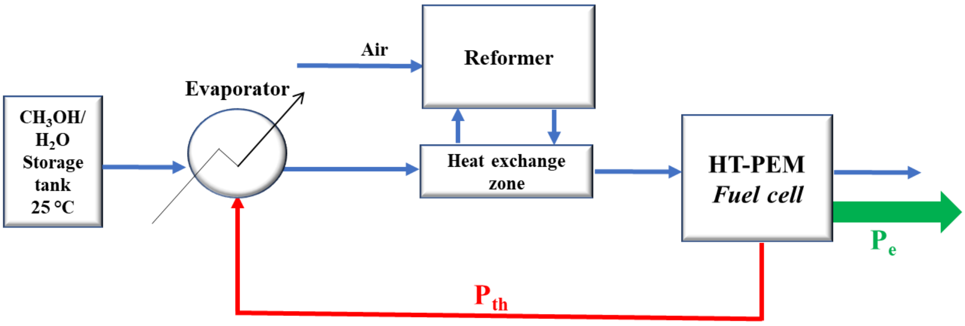

Figure 1: schematization of the methanol reformed fuel cell system

Figure 1 shows a schematic representation of the methanol-reformed fuel cell system. In order to determine the ratio of water to methanol required for the operation of the integrated system under autothermal conditions, simulations were carried out using Aspen Plus®. A preheating and evaporation stage for the reactant mixture and a steam reforming reactor for the methanol were considered, operating under adiabatic conditions (due to the addition of air) and thermodynamic equilibrium conditions. The calculations were performed using Gibbs free energy minimization under different operating conditions (calculations not given). From the results of the simulations, the value of the water-methanol ratio was set at 3. The safety of this mixture was first assessed by evaluating the flash point of the liquid mixture and the flammability limits of the gaseous mixture. Then, by applying the index method to the system (not reported), the tank containing this mixture was identified as one of the most critical units in terms of accident risk. For each tank failure, frequency analysis was performed based on properly developed fault trees (not reported). Starting from the initiating event, e.g. the formation of a hole in the tank containing the liquid mixture, the results were considered taking into account all the hazard-related factors. In the case of a continuous release of a liquid substance, the possible consequences are listed in Table 1.

Table 1: Possible outcomes due to the continuous release of methanol/water mixtures from the storage tank

Outcome	**Causes**
Toxic puddle	Accumulation of liquid on the ground and absence of the containment dike
Pool fire	Instantaneous ignition of the puddle
Toxic substance dispersion	Dispersion of not ignited substance
Flash fire	Delayed ignition of the cloud
Vapor cloud explosion	Delayed ignition of the cloud in the case of huge amount of substance well mixed with air

The consequences of the release of liquid from this tank due to the formation of a hole were studied and assessed by means of several empirical models (American Institute of Chemical Engineers - CCPS, 2000; Benintendi, 2021; Crowl and Louvar, 2002). In this work, the focus was on the effects of a vapour cloud explosion and comparisons were made between a methanol-water solution, methanol as such and gasoline, used in the conventional internal combustion engine. In particular, to assess the amount of gas in the explosive region of a vapor cloud released in the atmosphere, the model proposed by Van Buijtenen was used (Van Buijtenen, 1980). Moreover, to calculate the overpressure generated at different distances from the ignition point, the TNT model was used (Crowl and Louvar, 2002).

The results were compared with those of a tank containing gasoline. The tank volumes in the case of the conventional ICE with gasoline and the methanol-based system were determined assuming equality of the electrical power required for a ship engine and the navigation autonomy. Depending on the substance dispersed in the atmosphere, different dispersion models have been used to take buoyancy into account (American Institute of Chemical Engineers - CCPS, 2000; Crowl and Louvar, 2002).

3. Results

3.1 Safety features of the methanol-water mixture

To better understand the attenuating effect on flammability caused by the presence of water in the mixture, flash point of water/methanol mixtures was calculated by combining the Antoine equation for the vapour pressures and the condition of flammability on the water/methanol vapours (Crowl and Louvar, 2002). Notably, the flammability temperature or flash point is the lowest temperature at which vapours are formed in such quantities that, in the presence of oxygen (air) and an igniter, the gas mixture is flammable and may therefore explode (concentration of fuel equal to the lower flammability limit). If pure methanol was used, the flash point temperature would be 10.3 °C, so that the substance would burn very easily in the presence of an ignition. The presence of the inert substance, *i.e.* water, increases the flammability temperature. As the concentration of water in the mixture increases, the temperature rises in a range from about 10 °C to 57 °C, as shown in Figure 2a. Assuming the mixture is 75% water, the resulting flash point temperature is 29 °C.

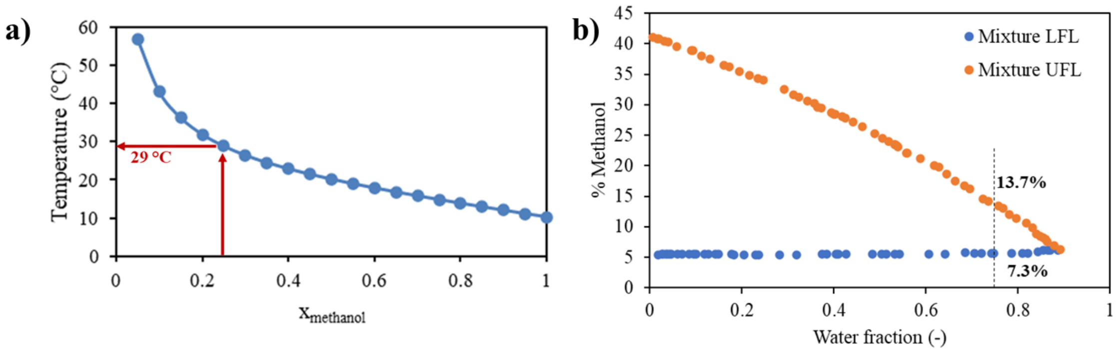

Figure 2: Trend of the flash point temperature as a function of the methanol fraction in the liquid mixture (a) and Lower and upper flammable limit of methanol depending on the water content in the gas mixture (Liaw et al., 2016) (b)

The nose diagram shown in Figure 2b was used to determine the flammability limits of the gaseous water-methanol mixture (Liaw et al., 2016). Since the molar composition of the mixture is 25% methanol, a sharp reduction in the flammability range is observed, which makes it possible to work with inherently safer conditions, but without completely eliminating the flammable and explosive effect of methanol. Indeed, the flammability range provides that the LFL remains unchanged and is 7.3%, while the upper flammability limit (UFL) decreases significantly, from 36% (in the case of pure methanol) to 13.7% (considering 75% water in the mixture). The results obtained are of considerable importance, because if the mixture had consisted of 20% or less methanol, it would not have been classified as flammable and a risk analysis would not have been necessary.

3.2 Consequence analysis

A case study inspired by the Seven Cruzeiro ship project was set up to compare a conventional diesel-fuelled combustion system with the methanol-based system (SubSea 7, 2023). The project includes a single diesel 35 m-long tank with a volume of 2197 m^3 and the presence of 6 engines of 3840 kW. The fuel on board allows an uninterrupted journey of 14 days. To ensure the same navigation autonomy, with a fuel cell efficiency of 50%, a complete methanol conversion and a hydrogen selectivity of 74%, 10000 m^3 of the methanol-water mixture must be provided. As reported in the International maritime organization (IMO) guidelines and regulations, the maximum capacity limit for oil fuel tank is set at of 2500 m^3 (International Maritime Organization (IMO), 2006). For this reason, in the case of methanol-water mixture, the presence of 4 vessels was considered. For both the system, the initiating event was considered to be the formation of a 50 mm diameter hole in the tank with continuous liquid leakage. In the case of the mixture, the failure of only one storage tank is considered and the effect of the domino effect on the other tanks is neglected at this stage. To illustrate the inerting role of water in the mixture, the results of a 2500 m^3 tank containing pure methanol are presented. The frequency of occurrence of this event is $5 \cdot 10^{-6}$ times per year (Lees, 1996), taking into account both the volume of the storage tank as well as the hole size. The mass flow rates exiting the hole are 9.4 kg/s, 11 kg/s and 9.2 kg/s for gasoline, methanol/water mixture and pure methanol, respectively. Due to the continuous release of liquid substance, it is possible the formation of a puddle. In case of immediate ignition of the vapours produced by the puddle, a pool fire may occur, whose damages are mainly due to the thermal flux caused by radiation. It should be noted that in the case of the water-methanol mixture, the likelihood of ignition is lower than for gasoline, as there is a large amount of water which acts as a heat sink and can prevent the flame propagation (Zhang et al., 2017). If the vapours are not ignited at the free surface of the puddle, they begin to disperse into the atmosphere. The mass flow rates are very low for all the systems ($2.9 \cdot 10^{-1}$ kg/s, $5.8 \cdot 10^{-4}$ kg/s and $1.2 \cdot 10^{-3}$ kg/s for gasoline, methanol/water mixture and methanol as it is, respectively), but the distribution is different due to the difference in buoyancy. The gasoline vapours tend to disperse downwards in the atmosphere because their density is higher than that of air. In contrast, when perfectly mixed in the vapor phase of the methanol-water mixture, these vapours tend to "float" in the atmosphere because their density is comparable to that of air. Different levels of concern (LOC) were considered for the two systems for flammability issues. The different LOCs as well as the distance at which they are realized are reported in Table 2. It is worth noting that the ranges of the flammable cloud, i.e. the distance between the upper and lower flammability limits, is only 10 cm for the methanol-water mixture, whereas it is about 20 m for diesel fuel. In any point of this range, therefore, ignition of the cloud is possible.

In the case of the mixture, ignition is therefore only possible in the area directly adjacent to the ignition source, whereas the flammable range for gasoline is much larger. Also important is the inerting role of the water in the mixture, which not only limits the flammable range of methanol alone, but also reduces the vapor pressure, resulting in a lower evaporation rate from the puddle than with pure methanol.

Table 2: Summary of the levels of concern and the distance at which they are realized for gasoline, methanol/water mixture and methanol itself

System	Levels of concern	Value (ppm)	Distance (m)
Gasoline	UFL	76000	14
	LFL	14000	36
	LFL/2	7000	58
Methanol/water	UFL	137000	0.4
	LFL	73000	0.6
	LFL/2	36500	0.8
Methanol	UFL	360000	0.04
	LFL	73000	0.8
	LFL/2	36500	1.2

If the dispersed cloud meets an ignition source with a sufficient energy content, this can produce an explosive cloud or a flash fire, depending on the degree of fuel-air mixing. The model formulated by Van Buijtenen was used to estimate the mass actually present in the flammable range and thus the mass actually involved in the explosion event (Van Buijtenen, 1980). This corresponds $2.8 \cdot 10^{-4}$ kg, $6.7 \cdot 10^{-10}$ kg and $1.2 \cdot 10^{-8}$ kg to for gasoline, methanol/water mixture and methanol as it is, respectively. This mass was then used in the TNT equivalence model in order to be able to estimate the effects of the overpressure conservatively. The overpressure trends determined for the various systems as a function of distance are shown in Figure 3. Starting from the ignition point, which is generally located at the LFL in a more conservative risk evaluation, the blast wave propagates in a radial direction and causes different damage depending on the system analyzed. As shown in Figure 3, the overpressure generated with gasoline vapours explosion is always greater than with the methanol-water (and pure methanol) system. In Table 3 the threshold values for the overpressure and the associated damage are given.

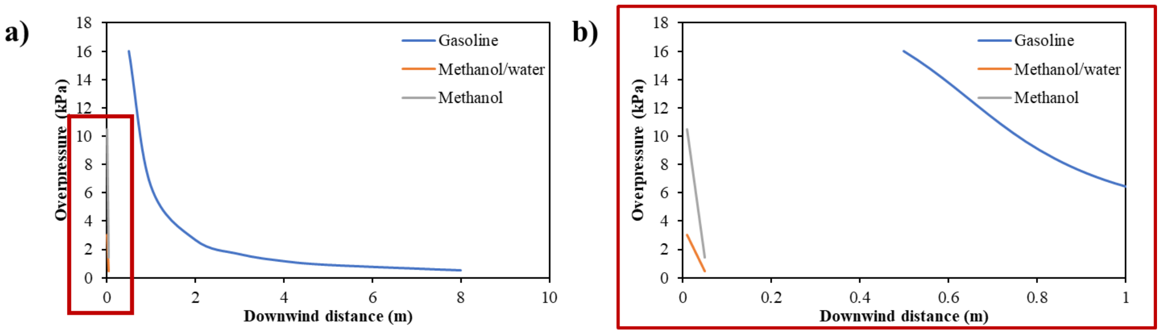

Figure 3: Overpressure trends (a) and their zoom (b) as a function of the downwind distance for gasoline (blue line), methanol/water mixture (orange line) and methanol (grey line)

The difference between the conventional and the methanol-based system in terms of impact and thus damage is evident. In particular, with the conventional system, severe damage to structures and people is possible even over distances in the meter range. With the methanol-based system, the damages are localized very close to the ignition point and has little impact. Here again, the inerting role of water is clear, which drastically reduces the overpressures realized in the case of ignition and explosion occurrence.

Table 3: Summary of the equations and the empirical models used for the consequences analysis

System	Overpressure (kPa)	Distance (m)	Damages
Gasoline	16	0.5	50% destruction of home brickwork
	2.7	2	Limited minor structural damage
	0.5	8	Loud noise (143 db); sonic boom glass failure
Methanol/water	2.7	0.01	Limited minor structural damage
	0.5	0.05	Loud noise (143 db); sonic boom glass failure
Methanol	10.5	0.01	Partial demolition of houses; made uninhabitable.
	1.4	0.05	Typical pressure for glass failure.

3.3 Preliminary risk considerations and domino effect

It is important to emphasize that a vapor cloud explosion is only possible if a large quantity of substance is present (Crowl and Louvar, 2002). In this case, the explosive mass of the substance present between the flammability range is strongly dependent on the vaporized mass from the puddles that is a function of the mass flow rate exiting from the tank, the equilibrium diameter of the puddle and the vapor pressure of the substance. In the case study investigated in this work, the explosive mass present in the atmosphere is very low and likely insufficient to account for the occurrence of a VCE. In this scenario, the most likely outcome could be a flash fire or, in the case of immediate ignition, a pool fire. Furthermore, when methanol is mixed with water, the parameters for the ignition probability are weakened compared to pure methanol. In particular, the presence of water increases the minimum ignition energy and the minimum ignition temperature (Zhang et al., 2017). As these parameters increase, the frequency of occurrence of VCE also decreases compared to gasoline. Data on ignition parameters for methanol and water vapours are not available in the literature, but as can be read in the literature, a high dilution with water (>70%) leads in the case of methane to a change in the minimum ignition energy from 0.2 mJ to 1.8 mJ (Zhang et al., 2017), which is thus higher than for vapor gasoline (0.8 mJ). Although the methanol-based system shows more contained results in terms of effects and damages than the traditional system, in future works, it is important to consider the occurrence of domino effects. Indeed, as previously described, to guarantee the same navigation autonomy as in the conventional case, a storage of 10000 m^3 of methanol-water mixture divided into four tanks is required. In the design phase, the occurrence of domino effects must be considered to predict the best position for the tanks and include compartmentation systems to reduce interaction in the event of an accident. To this aim, a multi-accident scenario probability model must be used in order to assess the consequences of the initial accident, highlight the accident chain, evaluate the occurrence frequency of units interactions and the final outcomes (Dueñas Santana et al., 2022; Zhang et al., 2019).

4. Conclusions

In the current energy scenario, the transition to the use of new technologies must necessarily be accompanied by assessments of sustainability, but above all of safety, to increase social awareness and acceptance. In this paper, preliminary risk considerations of the methanol-water storage integrated with the fuel cell unit and compared the results with those obtained with pure methanol and with gasoline used as feeding of conventional internal combustion engines. Particular attention was drawn to the mitigating effect of water in the solution on the flammability of methanol. In this work, the composition of the mixture fed to the reformer was set at 25% methanol and water. With this water-to-methanol ratio, not only the reformer operates at auto-thermal conditions, but also the whole system including evaporator, reformer and FC. In future works, it will be necessary to ensure that the feeding conditions obtained with this approach are still capable of guaranteeing high catalytic performance of the reforming reactor. The presence of 75% water in the mixture leads to a significant reduction in the flammability range, an increase in the flash point temperature and a reduction in the ignition probability. In the case of the occurrence of a vapor cloud, the difference between the gasoline and methanol-water storage systems is evident. In the former, the damage related to the overpressure can occur even at 10 m from the lower flammable limit, whereas in the latter, the effects and damage are localized and limited to the release zone and to 1 m away.

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