Hydroxylamine *vs.* Hydrogen Peroxide: a Comparative Study on Storage Stability

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The chemical industry often handles, stores, and processes molecules like hydroxylamine (HA) and hydrogen peroxide (HP), which can easily undergo thermal decomposition reactions. Hence, the ideal perspective is to have simple quantitative criteria to use during the equipment design phase, accommodating the possibility of exothermic degradations of substances to enhance process safety and avoid thermal runaways. To this aim, the Frank-Kamenetskii theory of self-heating (FKT) can be involved in determining the critical size of a storage vessel to guarantee the intrinsic safe storage of chemically hazardous materials.

Eventually, the proposed design strategy will be implemented to design storage equipment for two commercial aqueous solutions of HA and HP, respectively. In this way, it will be possible to compare the inherent thermal hazard linked to the storage of these mixtures, evaluating the threshold vessel size above which the self-heating phenomenon of the materials becomes no longer controllable. The HA and HP mixtures can be used alone or together in chemical processes as oxidants or precursors for producing hydroxyl radicals.

Under comparable conditions free of impurities and organic contamination, the results show that the system made of 50 %w hydrogen peroxide is more stable than hydroxylamine. This is reflected in a larger characteristic size of the storage vessel able to handle appropriately self-heating phenomena potentially leading to runaway.

1. Introduction

It is well known that runaway phenomena are one of the leading causes of devastating industrial accidents (Mocellin et al., 2022). According to the ARIA database (ARIA), in the last 10 years, 14 accidents due to uncontrolled exothermic reactions took place in France, which involved organic and inorganic compounds, pharmaceuticals, or lithium-ion-based systems. Moving to China, from 1984 to 2019, up to 271 industrial accidents were caused by runaway reactions, mainly related to organic compounds (57.2 %), inorganic molecules (10.7 %), pharmaceutical substances (7.0 %) and agricultural chemicals (6.6 %) (Zhang et al., 2021). This agrees with the reported literature for the French industry runaway accident analysis (Dakkoune et al., 2019). For what concerns the USA, the CSB database (CSB database) reports 13 industrial accidents under the section "reactive incident" from 2000 to 2023. The substances involved are mainly inorganic, pyrotechnic, and organic compounds. The companies belong primarily to the petrochemical, waste treatment, and fireworks manufacturing sectors, whereas the equipment involved were reactors, dryers, storage vessels and distillation columns. In the UK industry, from 1988 to 2013, 30 industrial accidents related to runaway reactions occurred (Saada et al., 2015). In these cases, polymerisation, decomposition, ethoxylation, refining, hydrogenation, and cracking processes were the primary sources of deviation from standard operating regimes and storage and transportation activities. Regarding the involved materials, fine chemicals, intermediate and heavy organics, plastics, rubbers, resins, and pharmaceuticals were the main responsible for uncontrolled thermal phenomena. Considering only the petrochemical industry, runaway reactions are the cause of almost 25 % of the total events of major accidents (Balasubramanian and Louvar, 2002).

Thus, to enhance process safety and system reliability, it is paramount to dispose of quantitative criteria to evaluate, manage and reduce risks related to exothermic reactions from the conceptual design of equipment to the standard operation of a chemical plant (Bassani et al., 2023). At the state of the art, to reduce the occurrence of these uncontrolled exothermic chemical transformations, primary attention is paid to the design (Andriani et al., 2024a) and operation (Vianello et al., 2018a) of chemical reactors. However, the risk of runaway can also be induced by an erroneous storage of chemicals caused by wrongly managed self-heating phenomena. Under this perspective, the Frank-Kamenetskii theory of self-heating (FKT) can be used to deeply understand the self-heating features to limit their devastating effects (Frank-Kamenetskii, 1955). Using FKT, it is possible to have a practical criterion to verify if a storage vessel has been well-designed to dispose safely of the thermal energy generated by an unwanted exothermic reaction.

Exothermic thermal decomposition is a typical unpleasant chemical process that must be accounted for when handling unstable materials (Pio et al., 2021). To understand the decomposition dynamic clearly, a classical strategy that could be implemented is performing a calorimetric analysis (Vianello et al., 2018b). With this experimental approach, it is possible to determine the main characteristics of the thermal degradation reaction, assessing thermodynamic, kinetic, onset and peak features. The calorimetric study of chemical reactions can be performed using different techniques, such as differential scanning calorimetry (DCS), thermogravimetric analysis (TGA), isothermal, adiabatic and reaction calorimetry, or accelerating rate calorimetry (ARC) (Vyazovkin et al., 2018). The main differences between the mentioned experimental strategies mainly consist of how the heat can be supplied to the system, the sample size and equipment, whether it is present or not stirring and the data acquisition procedure.

On one hand, with calorimetry, it is possible to retrieve reliable data related to decomposition reactions. On the other hand, the FKT can provide a well-grounded methodology for the basic design and analysis of storage equipment. The objective of this work is to explore the combination of experimental data acquisition and elaboration as a means of improving chemical process safety. This methodology has potential applications in the design of storage vessels for thermally unstable substances, in line with the principles of Inherently Safer Design. By enabling the management of self-heating phenomena that may occur during the storage of high holdups, this approach can significantly reduce the risk of runaway accidents. As an example, two different unstable mixtures will be considered as case studies: a 50 %w/w hydroxylamine (HA) and hydrogen peroxide (HP) aqueous solutions. These two materials can be used separately in a wide variety of chemical processes (Ullmann, 2011) or together to produce hydroxyl radicals, a versatile reactant for the synthesis of chemicals or the oxidation of recalcitrant and toxic species (Chen et al., 2015). The dependence of the decomposition behavior of the HP 50 %w/w related to the presence of impurities will also be assessed.

2. Methodology

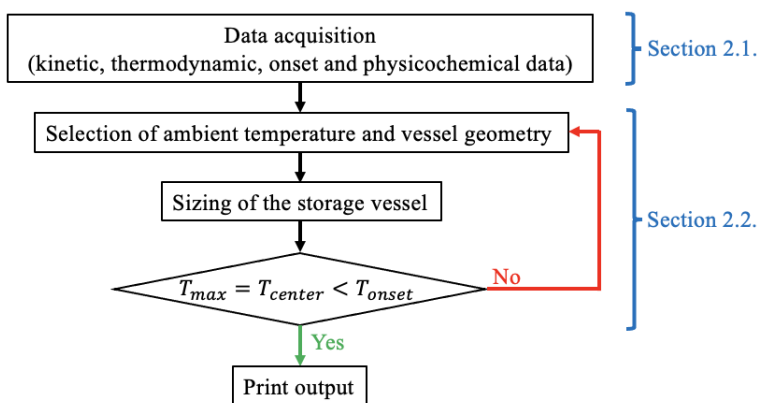The logic workflow of the methdology is reported in Figure 1.

Figure 1: Logical workflow of the proposed methodology.

2.1 Data acquisition

The preliminary step of the proposed method consists of acquiring the main physicochemical information. Being more specific, E_a, $k_{k\infty}$, n, C_{A0}, ΔH_r, T_{onset}, C_P and k_T are needed. All the quantities mentioned are necessary to model the decomposition of the 50 %w/w HA and HP aqueous mixtures. Onset temperatures, reaction kinetic

and thermodynamic data are resumed in Table 1. More specifically, the data related to the HP mixture has been taken from the literature (Anothairungrat et al., 2019) and in technical reports (Cefic Hydrogen Peroxide Technical Committee, 2021). Whereas the information belonging to the HA aqueous solution has been retrieved in the literature (Andriani et al., 2024b), in which a Thermal Screening Unit (TS[U]) calorimeter has been adopted for the kinetic studies.

Table 1: Kinetic, thermodynamic and onset data of decomposition reaction.

Mixture	E_a [J/mol]	$k_{k\infty}$ [s^{-1}]	n [-]	C_{A0} [mol/m^3]	ΔH_r [J/mol]	T_{onset} [K]
50 %w/w HA	$103 \cdot 10^3$	$9.33 \cdot 10^9$	1	$16.56 \cdot 10^3$	$-79.8 \cdot 10^3$	393.15
50 %w/w HP	$86 \cdot 10^3$	$1.94 \cdot 10^6$	1	$17.64 \cdot 10^3$	$-98.0 \cdot 10^3$	353.00

The possibility of accounting for contaminants inside the HP mixture is worth mentioning. This involves using cf to determine $k'_{k\infty}$, evaluated as the product between $k_{k\infty}$ and cf (Cefic Hydrogen Peroxide Technical Committee, 2021). Indeed, it is well known that HP is very sensitive to impurities (Wu et al., 2011). Metallic contaminants can catalyse the decomposition mechanism, while organic matter can generate additional thermal energy due to parallel exothermic oxidation reactions. Thus, quantifying the effect of contaminants on the stability of the mixture in terms of maximum safe equipment size will be worth noting.

2.2 Sizing of the storage vessel

The sizing methodology of storage vessels proposed in this section is based on the FKT, a complementary model of the Semenov theory (Babrauskas, 2014). In the FKT, a quiescent fluid is assumed to exchange heat with the environment only with a conductive mechanism. Additionally, under the assumption of Bi equal to infinity, the environment temperature can be considered uniform and constant, whereas, inside the system, a temperature distribution will be established. Under this perspective, the maximum temperature of the reactive material will be in the centre of the vessel. The governing equation of the FKT, reported in Eq(1), has been derived considering that, due to the idealised cylindrical geometry of the system, the dimensionless temperature depends only on time and radial coordinates. In addition, a negligible reactant conversion and E_a tending to infinity have also been assumed. Considering a storage vessel where an undesired decomposition reaction could occur, all the above assumptions will lead to a conservatively safe-side designed vessel. Indeed, the stored fluid can be considered almost quiescent, except for natural convective motion, which contributes to dissipating the heat generated by the exothermic decomposition reaction. Furthermore, considering the thermal degradation as a collateral effect during storage, only a tiny amount of material will be reasonably consumed.

$$r_{w,crit} = \sqrt{\frac{\delta_{crit} \, k_T \, R_g \, T_{amb}^2}{(-\Delta H_r) \, k_{k\infty} \exp\left(-\frac{E_a}{R_g T_{amb}}\right) C_{A0}^n \, E_a}} \qquad (1)$$

Concerning Eq(1), all the variables involved must be expressed in SI units and the value of δ_{crit} strictly depends on the system geometry. Being the storage vessel modelled as a cylinder, δ_{crit} = 2.00 and $r_{w,crit}$ = r. Then, once a reference value of T_{amb} has been selected, $r_{w,crit}$ can be easily determined, or vice versa. Furthermore, the physical meaning of $r_{w,crit}$, is linked to the ability of the system to handle the self-heating phenomenon. Indeed, for systems having a radius r > $r_{w,crit}$, the considered equipment will no longer be able to dispose of the thermal energy safely. Hence, the self-heating phenomenon will lead to a runaway. On the other hand, for every value of system radius r ≤ $r_{w,crit}$, a safe material's storage is ensured. As a further verification of the reliability of the proposed methodology, it is possible to check that T_{max} is lower than T_{onset}. Specifically, T_{max} can be quantified according to (Chambré, 1952).

3. Results and discussions

The results of the sizing methodology will be expressed in terms of $r_{w,crit}$ able to prevent runaway phenomena induced by self-heating features. Specific manuals must be consulted for a complete storage equipment design (API, 2020). From another perspective, the proposed strategy can be involved to verify that existing storage equipment containing materials prone to decomposition can safely handle the controlled substances.

3.1 Storage vessel sizing

Once all the physicochemical reference parameters of the materials have been collected and a specific geometry of the system has been set, a reference ambient temperature must be selected. Three different reference T_{amb} (i.e., 5 °C, 20 °C, and 35 °C) have been considered. A more detailed approach involves selecting a T_{amb} pertinent to the specific plant location or the maximum forecasted value. Table 2 reports the $r_{w,crit}$ and

T_{max} values as a function of T_{amb} for both mixtures. The reported values of $r_{w,crit}$ and T_{max} for the HP 50 %w/w aqueous mixture have been determined, neglecting the presence of impurities (i.e., cf = 1) and the thermal resistance offered by the equipment wall.

Table 2: Critical vessel radius and maximum reached temperature for both the HA and HP 50 %w/w water solutions as a function of the ambient temperature.

	$r_{w,crit}$ [m]		T_{max} [°C]	
T_{amb} [°C]	50 %w/w HA	50 %w/w HP	50 %w/w HA	50 %w/w HP
5	2.93	5.80	13.7	15.4
20	1.03	2.42	29.6	31.5
35	0.40	1.10	45.6	47.7

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Table 2, the first remarkable evidence is the strong dependence of the $r_{w,crit}$ from T_{amb}. Thus, the maximum credible ambient temperature must be carefully adopted for equipment design and verifications to ensure safe storage under seasonal variations. Considering a too low T_{amb} value, the risk of runaway will be underestimated due to an unproper-managed self-heating phenomenon of materials. Indeed, runaway scenarios are triggered if the system does not adequately dispose of the heat generated due to an exothermic reaction. In the presence of a homogeneous exothermic reaction, the Q_{gen} depends on V. Schematising the storage vessel as a vertical cylinder able to exchange heat with the environment only via A, the thermal power dissipated by the system depends on A itself. Under this perspective, the ratio V/A is representative of the ratio between Q_{gen} and Q_{ex}. Since V/A = r/4, when r increases, the relative weight of the Q_{gen}/Q_{ex} ratio will also increase accordingly. Thus, since a too-low reference T_{amb} results in a higher $r_{w,crit}$, a wrong assumption of T_{amb} will produce a vessel designed to be too prone to the runaway onset. In addition, analysing the listed T_{max} value, they are all far above the T_{onset} for both the mixtures, even if the highest value of T_{amb} is considered. This will ensure that the material will not undergo violent decomposition reactions even in the hottest period of the year.

Another interesting analysis concerns the stability of the HA and HP 50 %w/w aqueous solution. The storage of HP requires a critical vessel radius nearly double what is needed for HA, indicating the higher intrinsic instability of the HA 50 %w/w mixture as compared to HP, ignoring the presence of impurities. This bears significant implications for ensuring the safe storage of these chemicals and designing appropriate equipment accordingly.

3.2 Effect of the presence of impurities

As elucidated in Section 3.1., the HA 50 %w/w is more prone to decomposition compared to the HP 50 %w/w mixture. However, the thermal decomposition of the HP 50 %w/w aqueous solution can be enhanced by the presence of Fe^{3+} impurities. Therefore, it would be worthwhile to determine ω_{imp} that can trigger a decomposition reaction in the HP mixture. Even if both organic and metal impurities can increase the sensitivity toward thermal degradation of the HP, only the effect of metallic compound contamination will be further analysed. In addition, the metallic impurities will be modelled, assuming that they can be expressed in an equivalent amount of Fe^{3+} ions. From an industrial perspective, traces of metals can be found in the stored mixture because of welding defects, new pipeline installations or material transfer between containers if inline filters have not been properly installed. On the other hand, organic matter can enter the equipment from the atmosphere if filters in the lunging line of the vessel with the environment have not been predisposed or well installed. In summary, contaminants can reliably enter the equipment only in the presence of design, operational or maintenance errors.

As mentioned in Section 2.1, the impact of ω_{imp} on the decomposition kinetics of the HP 50 %w/w aqueous mixture can be measured using a corrective factor cf. When ω_{imp} increases, so does cf, resulting in a higher decomposition reaction rate and thus a greater amount of Q_{gen}. This, in turn, reduces the value of $r_{w,crit}$, allowing for better dissipation of the thermal power generated and preventing self-heating features from causing a runaway reaction. Figure 2 illustrates the trend of $r_{w,crit}$ as a function of cf for the HP 50 %w/w aqueous solution at an ambient temperature of 35°C. This trend will be compared to $r_{w,crit}$ obtained for the 50 %w/w HA to determine the value of cf that will equalize the critical vessel radius for both mixtures under analysis.
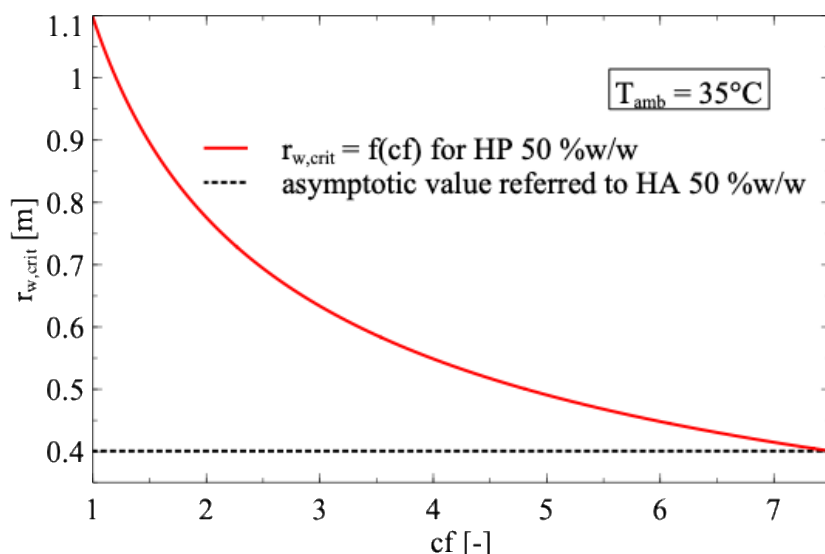
Figure 2: Critical vessel radius dependence on the kinetic corrective factor for the HP 50 %w/w aqueous solution compared to the value obtained for the 50 %w/w HA. Ambient temperature equal to 35°C.

Based on the data in Figure 2, it is possible to determine that to maintain the same level of stability against thermal degradation, both HP and HA 50 %w/w solutions with a cf value of 7.5 should be stored in equipment with a critical radius $r_{w,crit}$ of 0.40, assuming an ambient temperature of 35 °C. To refine this information further, ω_{imp} that corresponds to a cf value of 7.5 can be assessed using a correlation based on experimental data found in the literature (Cefic Hydrogen Peroxide Technical Committee, 2021). The analytical expression of the correlation is reported in Eq.(2), which is valid in the range $1 \leq cf \leq 7.76$ with R^2 of 0.99.

$$\omega_{imp}[mg/kg] = 2.361 \cdot 10^{-2}\, cf^3 - 2.027 \cdot 10^{-1}\, cf^2 + 6.509 \cdot 10^{-1}\, cf - 4.723 \cdot 10^{-1} \tag{2}$$

By utilizing the data extracted from Figure 2 and employing Eq(2), it has been quantified that the presence of 3.4 mg/kg of Fe^{3+} impurities can disrupt the stability of the HP 50 %w/w aqueous solution until it reaches the same level of decomposition as the HA 50 %w/w. Additionally, the decision to select the ambient temperature is based on the need for a storage container that can prevent thermal runaway throughout all seasons, requiring consideration of the highest anticipated ambient temperature value.

4. Conclusions

The present work outlines a methodology based on the FKT for designing storage vessels and evaluating the safety of existing equipment. To clarify its implementation, this methodology has been applied to two industrial mixtures (50 %w/w HA and HP) free from contaminants in aqueous solutions. Through the primary sizing methodology outcomes, it was determined that HP 50 %w/w is more stable than HA towards thermal degradation exothermic reactions, as the characteristic equipment size for safe storage is higher for HP.
However, it is worth noting that HP is sensitive to impurities. Indeed, in the presence of approximately 3.4 mg/kg of Fe^{3+} equivalent metallic contaminants, both materials exhibit the same decomposition tendency and $r_{w,crit}$ values. This underscores the importance of filters and safety barriers in preventing contamination scenarios and ensuring the safe storage of hazardous materials.

Nomenclature

A - lateral surface, m^2
Bi – Biot number, -
C_{A0} – initial main reactant concentration, mol/m^3
C_P – mixture's heat capacity per unit mole, J/mol K
cf – kinetic corrective factor, -
E_a – activation energy, J/mol
$k_{k\infty}$ – Arrhenius pre-exponential factor, s^{-1}
$k'_{k\infty}$ – corrected Arrhenius pre-exponential factor, s^{-1}
k_T – thermal conductivity, W/m K

n – reaction order, -
Q_{ex} - thermal power dissipated, W
Q_{gen} - thermal power generated, W
r – cylindrical equipment radius, m
R_g –universal gas constant, J/mol K
$r_{w,crit}$ –critical characteristic system dimension, m
T_{amb} - ambient temperature, K
T_{max} – maximum temperature reached in the bulk of the storage vessel, K

T_{onset} – onset temperature, K
V - system volume, m^3
δ_{crit} – critical value of the Frank-Kamenestkii number, -

ΔH_r – reaction enthalpy per unit mole, J/mol
ω_{imp} – quantity of Fe^{3+} impurities, mg/kg

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