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Innovative procedure for intrinsically safe storage vessel design: the case study on hydroxylamine decomposition

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Materials prone to exothermic decomposition reactions can generate severe concerns during storage activity on an industrial scale. Indeed, due to the large amount of handled chemicals, the consequences of runaway phenomena induced by improper management of the generated thermal energy could be devastating for the environment, people and assets. In the case of less extreme conditions, runaway reactions can be avoided, even if thermal degradation is activated by deviation in external conditions. Nevertheless, significant impacts on economic profitability and asset integrity should be considered. Indeed, during thermal degradation, valuable chemicals react and are converted into products that, in most cases, cannot be commercialised and require treatment and disposal as waste. In this view, the present work proposed an innovative procedure for simultaneously evaluating the safety and economic aspects, leading to a more sustainable and consistent way to conduct and design plants and equipment. This procedure is based on the Frank-Kamenetskii theory of self-heating (FKT), which can be employed for an intrinsically safe design of storage vessels handling molecules prone to exothermic decomposition reactions. However, in its original formulation, the FKT is not suitable for considering the effects of the activation energy of a reaction nor the consequence of reactant conversion on the overall self-heating dynamic. Under these premises, this article reports an expanded FKT to evaluate the effects of a simultaneous resolution of the energy and mass balance on the numerical outcomes of the theory. The obtained approach was applied to design storage vessels containing materials prone to exothermic degradation reactions. For the sake of validation purposes, numerical predictions obtained in this work were compared with experimental data available in the current literature on the decomposition of aqueous solutions containing hydroxylamine salt, showing an excellent agreement. Different compositions and external boundary conditions were tested to this scope. Therefore, the adopted procedure can be considered for the sizing of equipment containing chemicals, to efficiently dispose of the generated thermal energy, avoiding runaway conditions induced by a poorly managed self-heating mechanism.

* 1. Introduction

Runaway phenomena are widely recognized as a major cause of catastrophic industrial accidents (Mocellin et al., 2022). To enhance process safety and system reliability, it is essential to have quantitative criteria for evaluating, managing, and mitigating risks associated with exothermic reactions from the early stages of equipment design to the routine operation of an industrial plant (Bassani et al., 2023). Currently, considerable emphasis is placed on the design (Andriani et al., 2024a) and operation (Vianello et al., 2018a) of chemical reactors to prevent uncontrolled exothermic reactions. However, risks of runaway reactions can also arise from improper chemical storage due to mismanaged self-heating phenomena. In this context, the Frank-Kamenetskii theory of self-heating (FKT) provides valuable insights into self-heating characteristics, helping to mitigate their detrimental effects (Frank-Kamenetskii, 1955). Specifically, FKT offers a practical criterion for assessing whether a storage vessel is adequately designed to safely dissipate the thermal energy generated by unintended exothermic reactions. Numerically, FKT relies on the assumption of a quiescent fluid within a system having negligible wall thermal resistance (Bi→∞), minimal dimensionless thermal conductivity (χ→0), and nearly infinite dimensionless activation energy (γ = Ea/RgTamb→∞) (Boddington et al., 1983). For a static conductive fluid, the assumption of Bi→∞ is easily met without compromising model accuracy. Nonetheless, to broaden FKT's applicability, it is advisable to incorporate the effects of and reactant consumption on the critical Frank-Kamenetskii number (δcrit) used in storage vessel design and on the maximum reached temperature (Tmax) to further verify the reliability of the design outcomes.

Exothermic thermal decomposition is a common hazardous process to consider when handling unstable materials (Pio et al., 2021). To thoroughly understand decomposition dynamics, a classical approach involves conducting a calorimetric analysis (Vianello et al., 2018b). This experimental method enables the determination of key characteristics of thermal degradation reactions, including thermodynamic, kinetic, onset, and peak features (Vianello et al., 2015). Various techniques such as differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), isothermal calorimetry, adiabatic calorimetry, reaction calorimetry, and accelerating rate calorimetry (ARC) can be employed for such studies (Andriani et al., 2024b). Standard calorimetric analysis provides reliable data on decomposition reactions, while FKT offers a robust framework for the design and analysis of storage equipment. This study aims to explore the integration of experimental data acquisition and processing to enhance chemical process safety. This methodology is applicable to the design of storage vessels for thermally unstable substances, adhering to the principles of Inherently Safer Design (ISD). By effectively managing self-heating phenomena during the storage of large quantities of materials, this approach can significantly reduce the risk of runaway accidents. A case study involving a 30 %w hydroxylamine aqueous solution with 1 %w of hydroxylamine hydrochloride salt added, used in various chemical processes (Ullmann, 2011) or with H2O2 to produce hydroxyl radicals (Chen et al., 2015), will be presented. Storage vessels will be designed using the traditional FKT formulation, an expanded version considering the dependence of on , and a comprehensive model incorporating the mass balance equation to examine the impact of different modeling assumptions on the numerical results.

* 1. Methodology

Figure 1 illustrates the approach adopted in the current work.

 

*Figure 1. Schematic representation of the workflow adopted in the current work.*

* + 1. Data acquisition

The initial phase of the proposed method involves collecting key physicochemical data. Specifically, this includes the activation energy (Ea), Arrhenius pre-exponential factor (kk∞), reaction order (n), initial concentration of the main reactant (CA0), reaction enthalpy per mole (ΔHr), onset temperature (Tonset), heat capacity per mole of the mixture (CP), and thermal conductivity (kT). These parameters are essential for modeling the decomposition of a hypothetical mixture and sizing storage vessels with the FKT. The reaction kinetics, thermodynamic properties, and onset temperatures are summarized in Table 1. Other necessary correlations and numerical values have been sourced from existing literature (Andriani et al., 2024c). Experimental measurements for the kinetic, thermodynamic, and onset data for the 30 %w hydroxylamine with 1 %w hydroxylamine hydrochloride mixture were obtained using a Thermal Screening Unit (TSu) calorimeter, which facilitates ARC tests (Vianello et al., 2016).

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

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Ea [kJ/mol] | kk∞ [s-1] | n [-] | CA0 [kmol/m3] | ΔHr [kJ/mol] | Tonset [°C] |
| 103 | 9.33⋅109 | 1 | 16.56 | -79.8 | 127 |

* + 1. Storage vessel design

The sizing strategies of storage vessels proposed in this work are based on the FKT. However, in its original formulation, the FKT is based on several assumptions that may limit the accuracy of the design outcomes. For this reason, three different sizing algorithms will be elucidated in this section. The first is based on the canonical FKT formulation. The second one removes the assumption of a γ → ∞, allowing the determination a δcrit and Tmax values that fit the γ value under study. The last one removes both the assumptions of γ → ∞ and χ→0. In this way, more refined and realistic δcrit and Tmax values will be retrieved. Additionally, coupling mass and energy balances will make it possible to understand the trend of reactant consumption over storage time to plan the best storage practices to reduce economic losses due to the degradation of the stored material.

2.2.1 Standard FKT

In conventional FKT, it is assumed that a stationary fluid exchanges heat with its surroundings solely through conduction (Babrauskas, 2014). Furthermore, with Bi→∞, the ambient temperature is treated as uniform and constant, while a temperature gradient forms within the system. This implies that the highest temperature of the reactive material will occur at the center of the vessel. The FKT governing equation, shown in Eq(1), has been derived under the assumption that the dimensionless temperature depends solely on time and radial coordinates, given the idealized cylindrical geometry of the system. Additional assumptions include negligible reactant conversion and an infinitely high activation energy. These assumptions contribute to a conservatively safe design for a storage vessel where an unintended decomposition reaction might occur. Essentially, the stored fluid can be regarded as nearly quiescent, with natural convective motion aiding in the dissipation of heat produced by the exothermic decomposition reaction.

|  |  |
| --- | --- |
|   | (1) |

Regarding Eq(1), the value of δcrit is highly dependent on the system's geometry. For a cylindrical configuration, it is 2.00. Given that the storage vessel is modeled as a cylinder, the characteristic dimension of the system is the radius of the equipment. Once a reference value for Tamb has been chosen, rw,crit can be readily calculated, or vice versa. The physical significance of rw,crit relates to the system's capacity to manage the self-heating phenomenon. For systems with a radius r > rw,crit the equipment will be unable to safely dissipate thermal energy, leading to a runaway reaction. Conversely, if the system radius r ≤ rw,crit,, the material can be stored safely. To further validate the reliability of the proposed methodology, it is essential to ensure Tmax remains below Tonset. Specifically, Tmax can be calculated using Eq(2), with Θmax = ln4 in cylindrical geometries (Chambré, 1952).

|  |  |
| --- | --- |
|   | (2) |

2.2.2 FKT first expansion

The first proposed expansion of the canonical FKT aims to include the effect of γ on the δcrit and Θmax values. This expansion provides a more refined set of design and validation parameters, enhancing the robustness of the proposed design protocol and allowing further exploration of the consequences of assuming γ→∞ on the numerical results. To achieve this, the dimensionless 1D heat balance equation in cylindrical coordinates, as formulated in Eq(3), must be coupled with the corresponding sensitivity equation. The latter is derived by differentiating Eq(3) with respect to δ, yielding the normalized sensitivity expression given in Eq(4). These equations incorporate various dimensionless parameters, such as Θ, δ, = t rw2/α and Ω = r/rw, with their remaining definitions provided in Eqs(5) through (6).

|  |  |
| --- | --- |
|   | (3) |
|   | (4) |
|   | (5) |
|   | (6) |

2.2.3 FKT second expansion

In the second expansion of the FKT, it is necessary to eliminate the assumptions of γ→∞ and χ→0. To achieve this, a sensitivity analysis approach has been proposed. The transient dimensionless mass and heat balance equations used to determine the δcrit value for the process values under consideration is provided in Eqs(7) and (8), respectively. These equations includes various additional dimensionless parameters, such as Le = α/DAmix, and uA = CA/CA0 and B, whose definition is reported in Eq(9). The sensitivity equations involved can be obtained deriving the mass and heat balance by δ, being the formulation of the normalized sensitivity S(Θ; δ) the one provided in Eq(4).

|  |  |
| --- | --- |
|   | (7) |
|   | (8) |
|   | (9) |

2.2.4 Design procedure

The results of the sizing methodology will be presented in terms of rw,crit, which is a critical parameter for preventing runaway phenomena caused by self-heating. To determine this value, Eq(1) must be applied, and to verify it, the Tmax value obtained from Eq(2) should be compared with the Tonset value provided in Table 1, ensuring that Tmax < Tonset. However, implementing Eq(1) and Eq(2) requires prior knowledge of the δcrit and Θmax values. For the standard FKT, this is straightforward as constant values of 2.00 and ln(4) can be used for cylindrical geometries. In contrast, in the first expanded version of the FKT, δcrit and Θmax are functions of γ, and in the second refined version of the FKT, δcrit and Θmax are influenced by γ, Le, and B. Thus, in the first FKT expansion, a sensitivity analysis approach will be involved to retrieve the specific value of δcrit corresponding to the γ value under study. Conversely, in the second FKT expanded version, once γ, Le, and B are specified, δcrit and Θmax can be obtained through sensitivity analysis. Subsequently, after determining and verifying the rw,crit value, appropriate manuals should be referenced for the comprehensive design of storage equipment (API, 2007).

* 1. Results

After collecting all physicochemical reference parameters of the materials and establishing the specific geometry of the system, a reference ambient temperature must be selected. In this study, three different reference ambient temperatures (5°C, 20°C, and 35°C) were considered as representative of credible conditions. Prior to presenting the detailed results obtained from the application of the three FKT versions, Table 2 summarizes the adopted δcrit and Θmax values for the different ambient temperatures (Tamb).

Table 2: Critical Frank-Kamenetsky number (δcrit) and maximum dimensionless reached temperature (Θmax) adopted in the three formulations of the Frank-Kamenetskii theory for storage vessel design purposes.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | Tamb [°C] | γ [-] | Le [-] | B [-] | δcrit [-] | Θmax [-] | Θmax @ δcrit = 2[-] |
| Classical FKT | 5 | - | - | - | 2.000 | 1.386 | 1.386 |
|  | 20 | - | - | - | 2.000 | 1.386 | 1.386 |
|  | 35 | - | - | - | 2.000 | 1.386 | 1.386 |
| First expanded version | 5 | 59.96 | - | - | 2.038 | 1.425 | 1.171 |
|  | 20 | 56.89 | - | - | 2.040 | 1.430 | 1.166 |
|  | 35 | 54.12 | - | - | 2.042 | 1.435 | 1.162 |
| Second expanded version | 5 | 59.96 | 71.90 | 36.67 | 2.472 | 3.111 | 0.864 |
|  | 20 | 56.89 | 75.57 | 32.79 | 2.514 | 3.254 | 0.850 |
|  | 35 | 54.12 | 78.77 | 29.47 | 2.559 | 3.051 | 0.836 |

Examining the values presented in Table 2, it is evident that the value of δcrit increases across different FKT formulations. Introducing the effect of γ on δcrit, the critical FK number approaches an asymptotic value of 2 as the dimensionless activation energies increase. This trend aligns with the assumptions underlying the classic FKT formulation. A similar trend is observed for Θmax, which approaches an asymptotic value of 1.386 only for γ values approaching infinity. However, slight deviations between the two theories are noticeable for lower γ values, underscoring the necessity for a refined FKT formulation, especially for low dimensionless activation energies. Analysing the differences with the second expanded FKT version reveals more pronounced discrepancies. Although both δcrit and Θmax approach their asymptotic values with increasing γ, the values significantly deviate from those predicted by the classic and first expanded FKT theories. This deviation can be attributed to reactant consumption. The depletion of stored material reduces the reaction rate and, consequently, the thermal energy generated by the reaction. Therefore, the δcrit value above which runaway induced by self-heating occurs increases. Despite the increase in δcrit, Θmax also increases correspondingly. This indicates that while larger storage tanks can be designed without compromising industrial safety, the maximum temperature reached will be higher, increasing the likelihood of exceeding the Tonset value and failing the design verification. Another notable insight is the maximum dimensionless temperature reached for an FK critical number equal to that predicted by the standard FKT (i.e., δcrit = 2.00). The temperature reached with the two expanded versions of the FKT is significantly lower than the value predicted by the canonical FKT. This suggests that designing a storage tank using the basic FKT results in conservative equipment. For the same imposed boundary conditions, runaway induced by self-heating occurs at δcrit values higher than 2.00. Additionally, the maximum reached temperature is always lower than that required to meet the Tonset verification. Thus, the design's reliability is reinforced by both findings. However, if reducing the degree of conservativeness is necessary for better plant footprint utilization, a more refined FKT can be employed, ensuring safety and reliability of storage equipment. Once the dimensionless values of δcrit and Θmax are determined, the next step involves storage tank sizing and verification. The results obtained from all three FKT formulations are summarized in Table 3.

Table 3: Critical vessel radius (rw,crit) and maximum reached temperature (Tmax) detrmined with the three proposed formulations of the Frank-Kamenetskii theory.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Tamb [°C] | rw,crit [m] | Tmax [°C] | Tonset [°C] | Design status |
| Classical FKT | 5 | 47.11 | 11.43 | 127 | Validate |
|  | 20 | 11.02 | 27.14 | 127 | Validate |
|  | 35 | 2.971 | 42.90 | 127 | Validate |
| First expanded version | 5 | 50.11 | 11.61 | 127 | Validate |
|  | 20 | 11.40 | 27.37 | 127 | Validate |
|  | 35 | 3.001 | 43.17 | 127 | Validate |
| Second expanded version | 5 | 52.37 | 19.43 | 127 | Validate |
|  | 20 | 12.35 | 36.77 | 127 | Validate |
|  | 35 | 3.360 | 52.37 | 127 | Validate |

Critically examining the data in Table 3, the most notable observation is the strong dependence of rw,crit on Tamb. Therefore, the maximum credible ambient temperature must be carefully selected for equipment design and verification to ensure safe storage under seasonal variations. Using a reference ambient temperature that is too low will underestimate the risk of runaway due to improperly managed self-heating phenomena in materials. Another significant feature in Table 3 is the dependence of rw,crit and Tamb on the implemented FKT approach. For the same reference ambient temperature, as the degree of conservativeness of the theory decreases, the values of critical vessel radius and maximum reached temperature diverge. Consequently, the second expanded FKT version enables the design of inherently safer larger storage vessels, provided that a more stringent validation of Tmax compared to Tonset is conducted.

* 1. Conclusions

Storage vessels are critical industrial equipment where substantial quantities of hazardous materials can be stored. Therefore, ensuring the safety of these materials is paramount, especially when dealing with thermally unstable compounds. This study presents a methodology for determining an intrinsically safe system size to prevent runaway conditions caused by exothermic decomposition mechanisms. The methodology was tested using an inherently unstable mixture (aqueous solutions of 30 %w hydroxylamine with 1 %w hydroxylamine hydrochloride). To evaluate how the hypotheses underlying the method might affect design outcomes, three formulations of the Frank-Kamenetskii theory of self-heating (FKT) were employed. The results show good agreement among the three formulations. The least approximated formulation allows for the design of storage equipment that is at least 30% larger without compromising safety. Conversely, the standard FKT, which is less computationally demanding, still ensures safety as the maximum reached dimensionless temperature is at least 40% lower with the most detailed FKT version compared to the basic version. Future work will focus on a deeper analysis of the self-heating behaviour of unstable mixtures using the more detailed FKT version, aiming to produce stability and performance diagrams.

Nomenclature

B – dimensionless heat of reaction, -

Bi – Biot number, -

CA0 – initial main reactant concentration, mol/m3

CP – mixture’s heat capacity per unit mole, J/mol K

Ea – activation energy, J/mol

kk∞ – Arrhenius pre-exponential factor, s-1

kT – thermal conductivity, W/m K

Le – Lewis number, -

n – reaction order, -

r – cylindrical equipment radius, m

rw – equipment radius, m

rw,crit –critical characteristic system dimension, m

Rg –universal gas constant, J/mol K

 – reaction rate, kmol/m3 s

S(Θ;δ) – normalized sensitivity, -

t – dimensional time, s

Tamb - ambient temperature, K

Tmax – maximum reached temperature, K

Tonset – onset temperature, K

uA – dimensionless concentration, -

α - thermal diffusivity, m2/s

γ – dimensionless activation energy, -

δ - Frank-Kamenetskii number, -

δcrit – critical Frank-Kamenetskii number, -

ΔHr – reaction enthalpy per unit mole, J/mol

Θ - dimensionless temperature, -

Θmax – maximum dimensionless temperature,

νA – stochiometric coefficient of A, -

ρ – mixture density, kg/m3

χ – main reactant conversion, -

 – dimensionless time, -

Ω – dimensionless radius, -

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