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Article

Predicting the Autoaccelerating Hydrogen Peroxide Decomposition Rate after Mixing with Sodium Hydroxide

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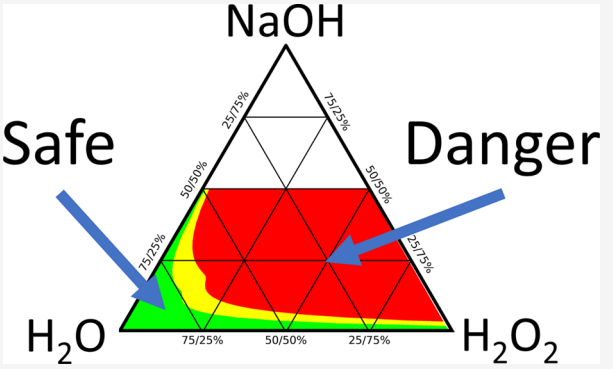
ABSTRACT: Due to the large amount of inherent chemical energy, implementation of hydrogen peroxide pulp bleaching requires a high level of safety design and process review. Even with safety controls, in-place accidents have occurred at kraft pulp bleaching facilities. Using a combination of experiments and chemical engineering analysis, we present a validated model of hydrogen peroxide decomposition under alkaline conditions that are typically found in kraft pulp bleaching processes. Using the model, we then calculated several characteristic parameters required to determine the criticality class and control system safety integrity level (SIL) for an industrial-scale bleaching process. When designed for 10 wt % hydrogen peroxide, pulp bleaching systems are inherently safe as long as it is used in a process with adequately sized pressure relief. Process designs using greater than 10 wt % hydrogen peroxide require controls with SIL 4, which is the highest level of control. This level is required for processes that present the most risk and have the most severe consequences. Regardless of the hydrogen peroxide concentration, processes without adequately sized pressure relief should never be considered safe. Finally, both the experimental and model results show the dramatic acceleration of hydrogen peroxide decomposition by iron. Because membrane-grade sodium hydroxide often has an order of magnitude lower concentration of iron than diaphragm-grade sodium hydroxide, choosing membrane-grade results in reduction in potential hazard.



INTRODUCTION

Hydrogen peroxide is a widely used, environmentally friendly, industrial chemical that has provided the energy behind several serious accidents.[1−5] Even though it is a potentially dangerous chemical, it has been used relatively safely as a bleaching agent for many decades. The current total global market for hydrogen peroxide is 4.8 million metric tonnes per year, with approximately half of it being consumed in the production of pulp and paper.[6] Pulp and paper mills are required to conduct extensive analyses and install systems and controls to mitigate the hazards presented by the storage and usage of hydrogen peroxide.[7] Under the guidance of the hydrogen peroxide supplier, mills implement safe operating practices, such as using only vented ball valves and Teflon-lined or acid-cleaned piping systems with no lubricant or organic fluxes employed during construction. Storage tank temperatures are continuously monitored, and unique hosepipe connections are provided to prevent unloading of other chemicals into the hydrogen peroxide storage tank. Prestart-up safety and hazardous material (HAZMAT) process reviews are required prior to the first filling of storage tanks and starting to use hydrogen peroxide in a process.

Hydrogen peroxide is covered by Occupational Safety and Health Administration process safety management (OSHA PSM) requirements when stored at a concentration of greater than 52% and a volume of more than 7500 gallons.[8] Most mills tend to purchase and store hydrogen peroxide at 50% concentration. Tanker car shipments above 60 wt % hydrogen peroxide are a DOT Class 5 substance. It is possible to receive hydrogen peroxide in rail cars at 70 wt % concentration but this material is diluted at unloading to about 50 wt % to avoid PSM storage requirements. Even though most mills store hydrogen peroxide at 50 wt % concentration, they still voluntarily use PSM guidelines and the 14 PSM program[9] without regulatory oversight. These guidelines include employee participation, process safety information, process hazard analysis, operating procedures, employee training, contractor training, prestart-up safety review, mechanical integrity (including periodic, documented inspections for pressure vessels, storage tanks, piping systems, and ventilation systems), hot work permits, management of change, incident investigation, replacement in kind, and emergency planning and response plan development.

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While mixtures of hydrogen peroxide and sodium hydroxide are potentially hazardous, normal operations can be considered safe because the mixture is diluted by pulp and water. Pulp mill-related accidents[5] that have occurred can be classified into two general causes. One, unintentional mixing of high-strength hydrogen peroxide with incompatible materials, for example, organic compounds, chealants, and transition-metal solutions. Two, process upsets resulting in collection of high-strength hydrogen peroxide and sodium hydroxide in the process equipment. Properly designing safety systems and controls are essential to preventing these accidents.

Mitigating the risks associated with the first kind of accident, that is, mixing with incompatible substances, is generally handled with operational controls. For example, making the hosepipe connections for off-loading hydrogen peroxide delivery trucks unique, so misconnecting them is difficult. Even with unique hose connections, there have been reported incidents where a truck driver and mill maintenance person have worked together and constructed an adaptor to unload the chealant into a hydrogen peroxide storage tank resulting in an explosion. In this specific accident, the chemical unloader remembered that the chealant was used with hydrogen peroxide and thought the two needed to be unloaded into the same tank.

Addressing the second cause of accidents, hydrogen peroxide collecting in equipment, is more difficult. Mechanical block valves are used to isolate the process from the hydrogen peroxide source during shutdown and maintenance conditions. These valves can leak as they age and at least one mill explosion was the result of a slowly leaking block valve allowing a pool of 50% hydrogen peroxide to collect in a pump during an extended outage. The cause of another explosion was that upon startup after an 8 h maintenance outage, partially dewatered pulp bridged above the mixing pump, which stopped the pulp flow. As this plant was designed to be completely upflow, there was only one pulp flow indication. The manufacturer assumed if pulp entered the front of the plant, it had to be flowing everywhere in the plant. Thus, peroxide flow was interlocked to a pulp flow meter, but that specific meter was located in the wrong spot to ensure pulp flow at the peroxide addition point. As a result, when the pulp flow stopped due to bridging, hydrogen peroxide and sodium hydroxide continued to flow and collected in the pump. Because of rapid autoacceleration, the heat and pressure could not be released quickly enough to prevent catastrophic failure of the pump housing, see Figure 1. Parts of the housing were recovered over a kilometer from the site.

When a pulp bleaching process is running, prevention of hydrogen peroxide buildup often relies on properly functioning sensors, electronic controls, and interlocks. A better approach to eliminate this second cause is to redesign the process to be inherently safe.[5] By reducing the concentration of hydrogen peroxide fed to the system and only allowing hydrogen peroxide addition after stock flow has been initiated and verified, one can greatly reduce the likelihood of control system failure leading to an explosion.

Improved understanding of chemistry can lead to better safety practices, but often it is accidents that drive innovation. In the 1980s, the codification of chemical risk analysis for thermal runaway reactions began.[10] Using chemical engineering principles to predict the behavior of chemical processes under conditions where a cooling failure occurred led to the development of criticality classes of various scenarios.[11] The term "criticality" is used in this analysis because the potential for thermal runaway can make the transition between safe and

Figure 1. Pulp mixing pump rotor after pulp explosion at a mill in Evadale, TX. For scale, the base of the rotor is approximately 65 cm in diameter.

hazardous operation occur over a rather narrow temperature range. Stoessel[11] defined five criticality classes based on the ordering of three temperatures that characterize the particular physical situation, MTSR = maximum temperature of the synthesis reaction, MTT = maximum temperature for technical reasons, and T_{D24} = temperature for which the reaction autoaccelerates within 24 h. Processes that present the most risk, Classes 4 and 5, are characterized by MSTR > T_{D24}, which means that there is enough chemical energy in the system to reach a temperature where autoacceleration can occur. The difference between class 4 and 5 is that MTT is below MSTR and T_{D24}, that is, a class 4 system is prevented from reaching an autoacceleration condition by some technical limit. In a class 5 system, the one presenting the most risk, there is no technical limit preventing the system from reaching the autoacceleration temperature.

Applying the criticality analysis to hydrogen peroxide bleaching requires translation of the relevant concepts. Specifically, under Stoessel's framework, the failure is assumed to be a loss of cooling. In the case of pulp bleaching, the failure is a loss of dilution and hydrogen peroxide accumulating in the equipment. In this case, the MSTR can be redefined to be the adiabatic temperature rise upon complete decomposition of hydrogen peroxide.

$$\mathrm{MSTR} = \frac{\frac{\Delta H}{M_w}P}{C_{p1} + (C_{p2} - C_{p1})P} + T_i \tag{1}$$

In eq 1, ΔH is the heat of decomposition of hydrogen peroxide, 94.8 kJ/mole;[12] M_w is the molecular weight of hydrogen peroxide, 34 g/mole; P is the weight fraction of hydrogen peroxide; C_{p1} and C_{p2} are the heat capacities of water and hydrogen peroxide, respectively, 4.184[13] and 2.628[14] J/g K; and T_i is the initial temperature. While this equation ignores the temperature dependence and the nonideal mixing rules for the heat capacity, it gives a sufficiently accurate result for the criticality analysis. To indicate the scale of the hazard, for a solution that has 50% hydrogen peroxide in water and an initial temperature of 20 ° C, MSTR = 426 °C. By inverting the equation, one can calculate that the hydrogen peroxide

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concentration that will reach 100 °C when starting from 20 °C is 11.6 wt %.

The details of a particular hydrogen peroxide incident depend on the physical design of the system. Beyond the potential pressure increase resulting from the solution reaching its boiling point, decomposition results in the production of one-half mole of oxygen per mole of hydrogen peroxide. This production of oxygen can also result in a fire hazard, which will not be considered in this study. Because of generation of gas, whether the physical system has sufficient venting determines the MTT, as presented above. In an open or sufficiently vented system, the MTT is likely the boiling point of the solution. As more heat is evolved, it is removed by evaporating water or hydrogen peroxide. For closed systems, the MTT may not be actively controlled, which can result in releases through rupture disks or catastrophic failures as described above.

Finally, turning to the autoacceleration temperature (T_{D24}), determining the temperature where the system autoaccelerates requires a sufficiently accurate kinetic model of the decomposition reaction. Because of industrial importance and wide availability, hydrogen peroxide decomposition is often used as a representative exothermic reaction.[12] For example, Wu and Qian[2] used hydrogen peroxide decomposition as a representative reaction to demonstrate the utility of their calorimeter. They also illustrated the hazards of a pressure pulse during the reaction in a closed system.

As we have discussed previously,[5] the kinetics of decomposition of hydrogen peroxide in an aqueous alkaline solution appears to be a bimolecular reaction between H_2O_2 and its conjugate base OOH^-, the perhydroxyl anion.[15] In addition, and often complicating kinetic analyses, common transition metals catalyze the decomposition. Abbot and Brown[16] have observed that the iron-catalyzed reaction is generally first order in hydrogen peroxide concentration but has a complicated relationship to the speciation of iron, which depends on the concentration, pH, and the age of the iron solutions. While many other transition metals are effective at catalyzing the decomposition of hydrogen peroxide, our ICP analysis of commercially available sodium hydroxide showed nondetectable levels of Co, Cr, Cu, Mn, and Ni.[5]

The purpose of the current study is to develop a kinetic model for hydrogen peroxide decomposition under conditions that are industrially relevant to pulp bleaching. We are augmenting our previous experiments[5] with choices of hydrogen peroxide concentrations that do not exhibit autoacceleration, which reenforces the conclusion that by limiting the concentration, hydrogen peroxide bleaching of pulp can be made inherently safe.

MATERIALS AND METHODS

The source of chemicals, experimental methods, and data acquisition were described in our previous study.[5] As stated above, the goal of this study is to conduct experiments under conditions that are similar to industrial bleaching conditions. If the aim was to obtain accurate thermal chemical properties of this reaction, we would use calorimeters like those previously described.[2,17] This study describes a model that not only includes the heat of reaction but also the heat losses in a typical system. To develop such a model, we require an estimate of the heat capacity and vapor pressure of the water−hydrogen peroxide−sodium hydroxide system over a wide range of compositions. While binary mixtures of sodium hydroxide−water[18,19] and hydrogen peroxide−water[21,22] have been thoroughly studied, the ternary system because of its inherent instability has not been studied. Thus, we need to make some assumptions about the properties of three-component mixtures based on the data obtained for the two-component mixtures.

Sodium Hydroxide−Water. Because of its industrial importance, the binary mixture sodium hydroxide−water has been extensively studied.[18−20] Several studies have determined the heat capacity as a function of composition and temperature. In addition, the international water properties correlation can be used to augment the data set with properties of pure water.[13] A total of 155 data points for heat capacity of mixtures spanning 0−191 °C and 0−71 wt % NaOH were used to develop a mixed polynomial expression, third order in temperature, fourth order in concentration, and one mixed term. The coefficients are given in Table 1. C_p is in kJ/kg K, temperature is given in °K, and concentration is given in weight percent. The significance of coefficients for the empirical model was tested using a nested F-test[23] and only those that were significant at $p < 0.05$ were used. These data provide model accuracy within 0.02 kJ/kg K root mean square (RMS) difference.

Table 1. Coefficients for NaOH−Water Heat Capacity (kJ/kg K) Correlation with *T* in K and *C* in wt %

A	4.183140
*T*1	-1.591450×10^{-3}
*T*2	$3.197444\text{E} \times 10^{-5}$
*T*3	-1.024832×10^{-7}
*C*1	-6.456482×10^{-2}
*C*2	2.802718×10^{-3}
*C*3	-5.376365×10^{-5}
*C*4	3.282450×10^{-7}
CT	-2.748829×10^{-5}

Hydrogen Peroxide−Water. Similar to sodium hydroxide, hydrogen peroxide is also an industrially important chemical and studies of the thermal physical properties of mixtures of hydrogen peroxide and water have also been conducted. For example, Giguére and Carmichael[14] studied the heat capacity of hydrogen peroxide−water mixtures between 25 and 60 ° C. Their observations suggest that if one accounts for the difference in molecular weight between hydrogen peroxide and water, these mixtures can be approximated as ideal. On a molecular level, this suggests that the hydrogen bonding structures of the solutions are similar to the pure components. There is a slight increase in the heat capacity of hydrogen peroxide due to the addition of internal degrees of freedom associated with the oxygen−oxygen bond. Using water as a basis and correcting for the difference in molecular weight of 18/34, one would predict the heat capacity at 0 ° C for hydrogen peroxide to be 2.214 kJ/kg K. The experimental value is 2.627 kJ/kg K.[14] Thus, over the range of conditions used in these experiments, one could approximate the heat capacity of water−hydrogen peroxide mixtures as a linear interpolation between the pure component values. This approximation results in a less than 8% error in the estimate of heat capacity.

Sodium Hydroxide−Hydrogen Peroxide−Water. As is demonstrated in the experiments described here, mixtures of sodium hydroxide, hydrogen peroxide, and water are unstable, and thus, experimental data on the heat capacity and thermal properties of these mixtures do not exist. Because hydrogen peroxide exhibits a hydrogen bonding structure in solution like that of water, we will assume that the thermal properties of

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sodium hydroxide in hydrogen peroxide and water will have the same composition and temperature dependence of sodium hydroxide in pure water, and the majority of the impact of hydrogen peroxide is to change the apparent molecular weight of the solvent. Eq 2 was used to approximate the heat capacity of the solutions over a range of compositions and temperatures in this study. Table 1 contains the values of the coefficients for this equation.

$$C_p = A \times (1 + (0.628 - 1) \times P/100) + T1 \times T + T2 \times T^2 + T3 \times T^3 + C1 \times C + C2^{\times}C^2 + C3 \times C^3 + C4 \times C^4 + CT \times C \times T \quad (2)$$

where C_p is expressed in J/g C, T in °C, and C and P in wt %.

Model Equations. To develop a predictive model for the time course of the decomposition of hydrogen peroxide, we used simple energy and mass balances to obtain the rate equations. Because the experimental reactions were run in insulated dewars, the only heat losses associated with the system are evaporative cooling and thermal mass of components in contact with the reaction mixture. For the purpose of this study, we assumed that the decomposition of hydrogen peroxide follows two mechanisms. One is the anion-neutral reaction. The other is an iron-catalyzed reaction; thus, the hydrogen peroxide rate equation has two sets of terms. These rate equations were assumed to have an Arrhenius form with activation energy values taken from the literature.[17,24] The heat of decomposition was also set at a literature value.[12,25] While the heat of dilution and heat of mixing of these solutions resulted in an increase in temperature, often amounting to 10−15 ° C, they are not considered in the rate equations. The starting point for the reaction is assumed to be the temperature to which the solution arrives after mixing. Under the conditions of these reactions, the deprotonation of hydrogen peroxide is significant. For the purpose of this analysis, the acid−base reactions were assumed to be faster than the other reactions in the system, and thus, the anion and neutral concentrations are assumed to follow the equilibrium expression characterized by K_a.[26] The temperature dependence of K_a was ignored. Following these assumptions, eqs 3−8 were used to predict the temperature and mass of the system as a function of time.

$$(MC_p + M_{other})\frac{dT}{dt} = \Delta H\frac{[\ _t]}{dt} - E_l\Delta H_v P_{sat} \quad (3)$$

$$\frac{d[P_t]}{dt} = -(2e^{(\ln A_a - E_a/RT)}[P_a][P_n] + e^{(\ln A_{Fe} - E_{Fe}/RT)}[P_t][Fe]) \quad (4)$$

$$\frac{dM}{dt} = -E_l P_{sat} + \frac{32\ 34}{68}\frac{d[P_t]}{dt} \quad (5)$$

$$[P_t] = [P_a] + [P_n] \quad (6)$$

$$K_a = \frac{[P_a][H^+]}{[P_n]} \quad (7)$$

$$[H^+] = \frac{K_a([P_t] - [NaOH]) + \sqrt{(K_a([P_t] - [NaOH]))^2 + 4K_aK_w[NaOH]}}{2[NaOH]} \quad (8)$$

Definition of terms:**Variables:** T = temperature (K), t = time (s), M = mass (g), $[P_t]$ = total hydrogen peroxide concentration (moles/L), $[P_a]$ = peroxide anion concentration (moles/L), $[P_n]$ = hydrogen peroxide neutral concentration (moles/L), $[H^+]$ = proton concentration (moles/L), [NaOH] = sodium hydroxide concentration (moles/L), C_p = heat capacity of the mixture (J/g K) see discussion above. P_{sat} = saturation vapor pressure of the mixture[13] (MPa), ΔH_v = 3166.91391 − 2.43245245 × T (J/g) = heat of vaporization (note T in is K) **Set Parameters:** E_a = 95,000 (J/mole) = activation energy of the anion-neutral reaction, E_{Fe} = 75,000 (J/mole) = activation energy of the iron-catalyzed reaction, ΔH = 94,800 (J/mole) = heat of decomposition, R = 8.314 (J/mole K) = gas law constant, $K_a = 2.24 \times 10^{-12}$ (mole/L) = weak acid disassociation constant for H_2O_2, $K_w = 1.65 \times 10^{-14}$ (mole/L)^2 = disassociation constant for water **Fit Parameters:** $\ln A_a$ = 22.914 = natural log of the pre-exponential factor for anion-neutral reaction, $\ln A_{Fe}$ = 19.125 = natural log of the pre-exponential factor for iron-catalyzed reaction, M_{other} = 500 (J/K) = heat absorption of the calorimeter, E_l = 0.2534 (g/s MPa) = evaporation mass loss per MPa of vapor pressure.

Numerical Solution of Model Equations. Given the complexity of the model, advanced numerical methods are required to integrate the rate equations. We used two approaches. The first approach was based on the SUNDIALS package using the CVODE solver.[27] The rate equations were coded in C++ using Visual Studio and compiled to an executable DLL, which was linked to MS Excel. The second approach was based on Python 3.9 and the implementation of the modules was found in NUMPY and SCIPY. The Python codes for these implementations can be found in the Supporting Materials. The C++ code and Excel files can be obtained upon request from the authors. With both approaches, similar results were obtained. The solver function in Microsoft Excel and the module LMFIT in Python were used to determine the values of adjusted parameters that minimize the error squares. Temperature was recorded once every second for 26 compositions. The combined data set included 33,000 individual temperature readings. The minimum values for both the Excel and Python models for the fitted parameters agreed and resulted in an RMS error of 0.13 °C.

Two observations about the fitting procedure can be made. First, the model does not completely account for the heat losses as the solutions approached their boiling point, so the data fit was limited to 96 °C. Second, there appears to be variations in the amount of iron catalysis occurring in the systems. No attempt was made to fastidiously acid wash the equipment between runs and thus a factor was added to the fitting equations, which allowed for small variations in the iron concentration. The average value of this factor was 1.0.

For the purpose of generating an estimate of T_{D24}, the starting temperature of a particular mixture was set at 0 °C and then stepped up by 0.25 °C until the temperature exhibited a temperature rise.

Generation of Ternary Plots. Using the fitted values described above, the model was exercised over a range of compositions. Upon obtaining lists of these values, the contour plotting functions in the Matplotlib Python module were used to generate contour plots in the ternary plots found in this study. The codes to generate these plots are found in the Supporting Materials.

RESULTS

One output of the model is the predicted adiabatic temperature rise. A contour plot on a triangle diagram of the adiabatic temperature rise is shown in Figure 2. In this figure, the pure

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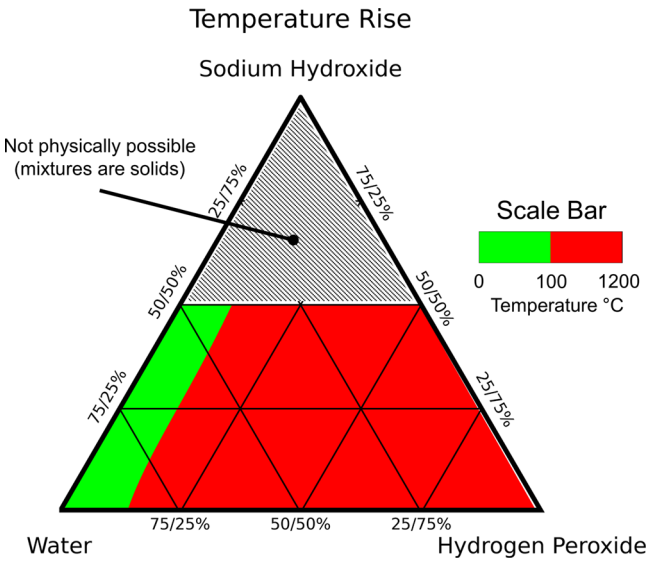

Figure 2. Potential adiabatic temperature rise as predicated by the model equations.

component compositions are represented by the vertexes of the triangle. The domain above the 50% sodium hydroxide line, the triangle with crosshatches, is a region where the mixture is likely a solid, at typical operating temperatures, and thus is not a physically relevant composition. The industrially relevant conditions are in the lower left corner near the water vertex. For the purpose of this figure, the transition of red to green regions was chosen to be 100 °C.

Inspection of Figure 2 shows that, as suggested by the analysis of eq 1, at sufficiently low concentrations of hydrogen peroxide, the thermal mass of the mixture is sufficient to prevent the temperature from rising more than 100 °C. While operating in this region is safer, the reaction mixture will still evolve oxygen, and thus, a closed system can reach failure condition due to pressure.

The predicted adiabatic temperature rise is strictly a function of the thermodynamic properties of the system. Because the model includes reaction rate expressions, it is possible to follow the temperature course of the reaction starting with various compositions and temperatures. To represent the potential hazards, the time to reach 100 °C was calculated. Figure 3 shows the results of model predictions plotted as contours on a triangle diagram, similar to Figure 2. For the purpose of this figure, the transition between the yellow and green regions of the contours was chosen to be 1200 s or 20 min, and between red and yellow, the transition was 400 s. Also displayed in Figure 3 are temperature versus time plots for three different compositions used in the physical experiments. The difference between the various time course plots is the initial concentration of hydrogen peroxide added to the mixture. Notice that the time course of the experiment with 11% hydrogen peroxide, Figure 3B, shows only a slow decrease in temperature, indicating that the heat lost by evaporation exceeds the heat generated by the reaction.

Turning to the time course of the experiment with 33% hydrogen peroxide, Figure 3A, one can observe that by 500 s, both the experiment and the model are approaching 100 °C. A close inspection of this figure shows that the heat loss in the model is insufficient to describe the heat loss as the system approaches boiling. This discrepancy is likely due to the convection associated with bubble formation, which would be difficult to include in the model. Given the ever-increasing slope as the temperature approaches 100 °C, clearly this composition results in an autoaccelerating reaction. Finally, the time course of the experiment with 50% hydrogen peroxide, Figure 3C, shows rapid autoacceleration by 100 s.

Except for deviations near boiling, likely caused by convection, the model accurately predicts the experimental data with an average RMS temperature difference over the 26 conditions used in this set of experiments of 0.13 °C.

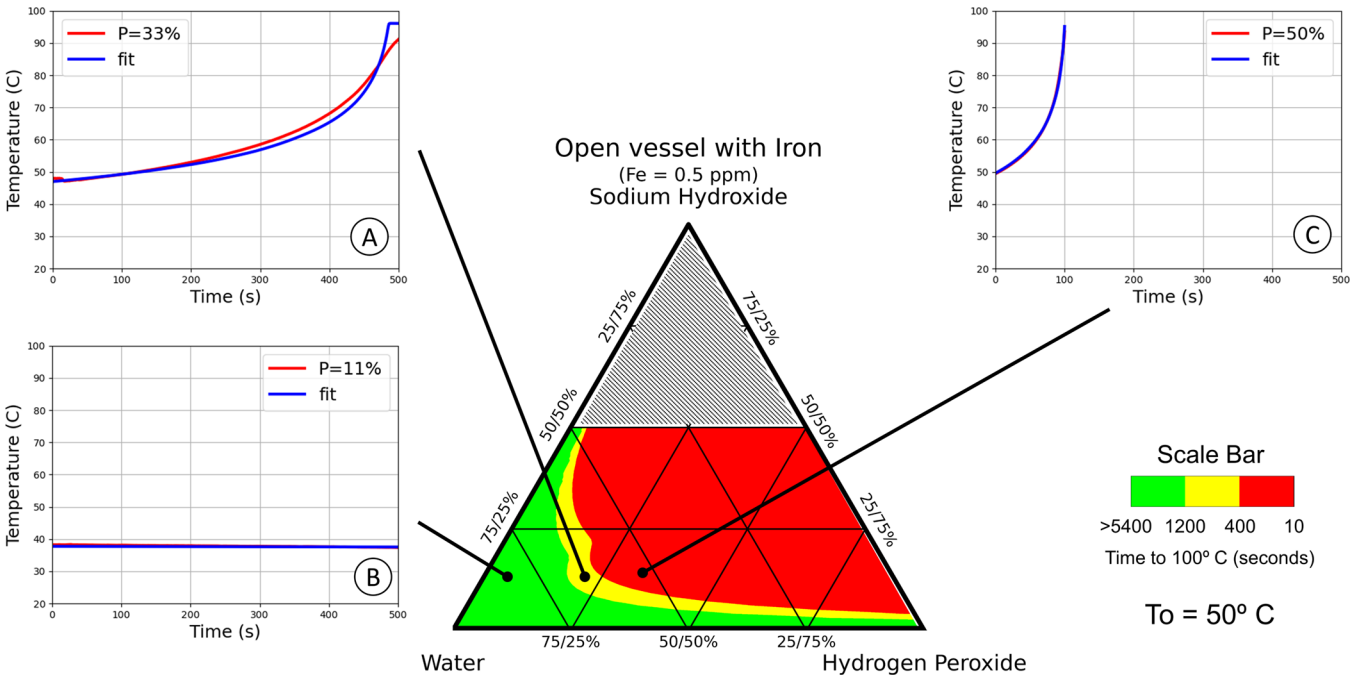

Figure 3. Comparison of temperature rise curves with the predictions from the model for various positions on the composition triangle diagram.

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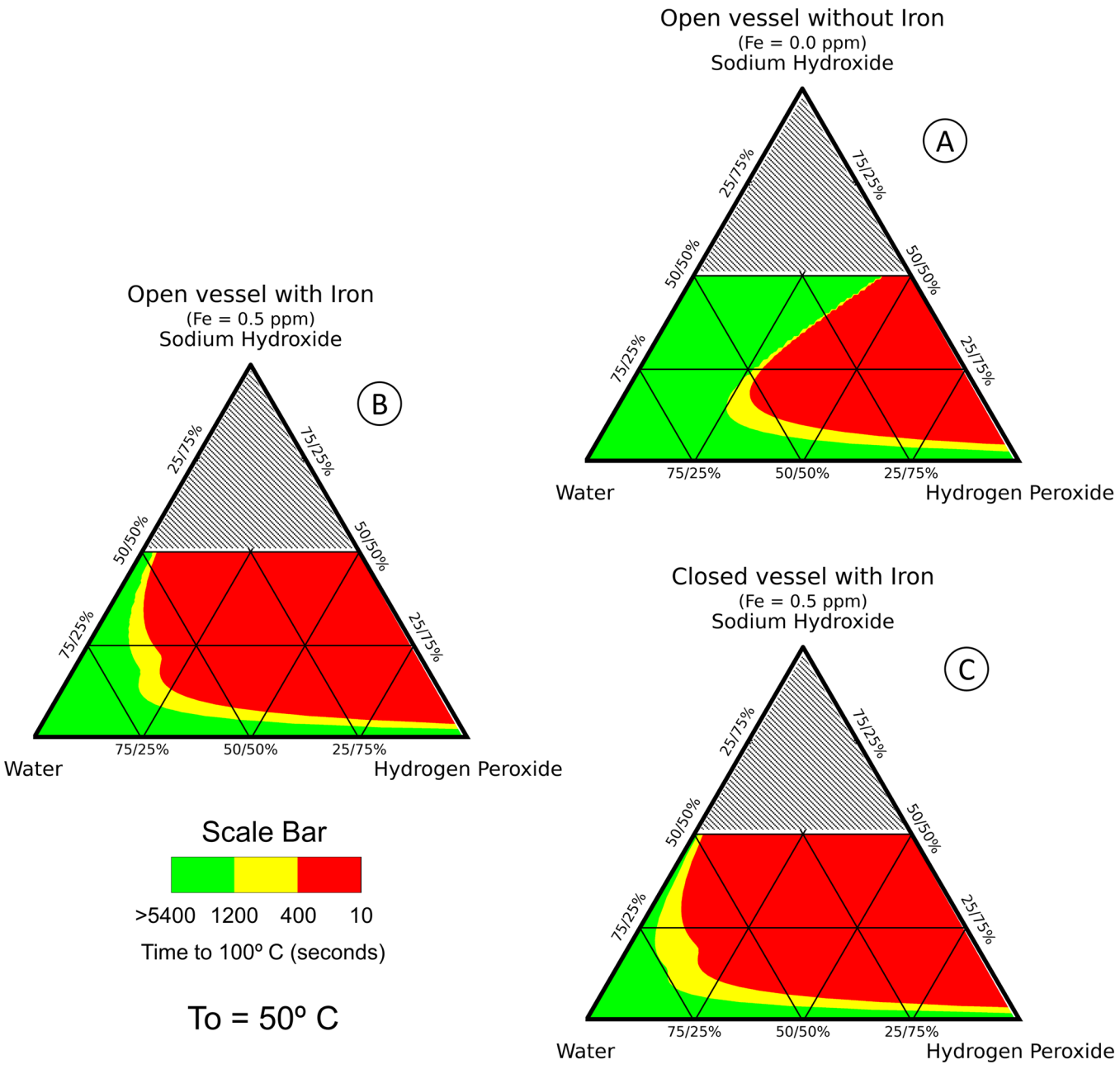

Figure 4. Time to reach 100 °C for various mixtures of hydrogen peroxide, water, and sodium hydroxide.

Given that the model appears to accurately represent the time course of experimental conditions, with some confidence, we can make predictions about conditions that were not experimentally tested. Specifically, we can investigate the impact of iron catalysis and evaporative heat loss. Figure 4 shows a composite of three ternary plots. Figure 4B is same as the triangle diagram shown in Figure 3 and represents an experimental condition of an open reactor with a concentration of iron that is typically found in commercial membrane-grade sodium hydroxide solutions. The other two ternary plots in Figure 4 represent two other conditions, namely, the cases of no iron catalysis in an open vessel, Figure 4A, and iron catalysis in a closed vessel, Figure 4C. Inspection of Figure 4A clearly shows that the region of potentially hazardous conditions is greatly reduced when the system does not include iron. One interpretation of this diagram is that, if it was possible to eliminate iron from the system, one could reduce the hazard. Given that all commodity sodium hydroxide contains some iron, eliminating iron would not be a reasonable hazard mitigation strategy for paper mills. In addition, they should resist the temptation to use lower quality, and typically lower cost, chemicals, that is, diaphragm-process sodium hydroxide, because they will contain higher amounts of iron. In the case of the closed system, with iron, we can observe that reducing the evaporative loss of heat enlarges the domain of hazard. This diagram likely best represents the hazard associated with the mill explosions described above.

The kinetic model was used to calculate the initial temperature at which a mixture will first exhibit the autoacceleration behavior (T_{D24}). Figure 4 shows a contour plot of T_{D24}. Figure 5 is different from the previously presented ternary plots in that only the lower left vertex is shown, the one

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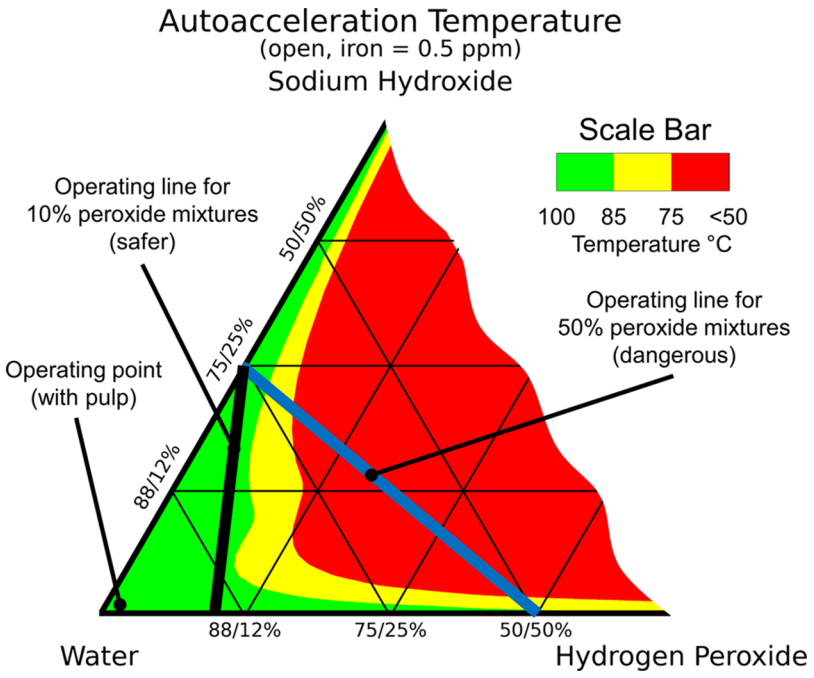

Figure 5. Temperature (T_{D24}) at which the various mixtures of hydrogen peroxide, water, and sodium hydroxide exhibit autoacceleration. Also shown are the operating lines for hydrogen peroxide mixtures of either 10 or 50 wt %. The indicated operating point is the concentration where pulp bleaching is conducted.

including the water vertex. This region of the triangle diagram contains all of the concentrations relevant for pulp bleaching. Also shown in the plot is the location of the typical operating point for pulp bleaching after the dilution resulting from mixing with pulp.

Figure 5 shows two operating lines. The operating lines connect 25% sodium hydroxide and two concentrations of hydrogen peroxide of 10 and 50%. When considering the hazards presented by mixing sodium hydroxide with various concentrations of hydrogen peroxide, operating lines are a useful construction. Any mixture of 25% sodium hydroxide with 10% hydrogen peroxide will lie on the operating line that connects these two starting concentrations on the triangle diagram.

Inspection of Figure 5 shows that the operating line for mixtures of 25% sodium hydroxide and 50% hydrogen peroxide crosses into the region where the temperature at which the mixture autoaccelerates is less than 50 °C. The mill explosions described in the introduction likely were on this operating line. In contrast, if hydrogen peroxide is diluted to 10%, the operating line does not pass through this region and the process is inherently safe, as long as it is sufficiently vented.

Returning to the criticality analysis of Stoessel,[11] the kinetic model allows one to calculate T_{D24} and MTSR. In this particular case, the MTT is assumed to be the boiling point, 100 °C, because the system is open and sufficiently vented. Figure 6 shows these temperatures as a function of the initial hydrogen peroxide concentration, assuming a constant value of sodium hydroxide and iron concentration. For hydrogen peroxide concentrations below 10%, MTSR is below the MTT and the reaction never autoaccelerates, so this region is not assigned a criticality class, that is, the loss of control is unlikely. For hydrogen peroxide concentrations above 10%, the T_{D24} is below MTT, and thus, the criticality class is 4. The fact that typical operating temperatures are above T_{D24} suggests that this system presents an even greater risk of autoacceleration, which is a condition that Stoessel did not consider.

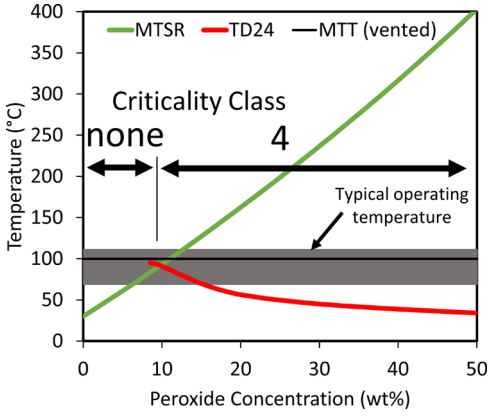

Figure 6. Determination of criticality class for open or sufficiently vented hydrogen peroxide systems. The values in this figure were calculated assuming 8% NaOH and 0.5 ppm iron.

DISCUSSION

Over the last 50 years, hundreds of millions of tons of hydrogen peroxide have been used for pulp bleaching. Over this same time period, there have been relatively few catastrophic events associated with hydrogen peroxide use. Clearly, the pulp and paper industry has done a good job of mitigating the hazards associated with the use of hydrogen peroxide in bleaching, but the fact that any incidents have occurred suggests that the industry is still at risk and can continue to improve.

To conduct a complete risk assessment for a particular process, one begins by determining the criticality class, which was accomplished for open systems using the kinetic models that have been developed for this study. The next steps in risk assessment involve more general considerations, for example, probability, severity, likelihood of control, energy density, and gas generation. When considering hydrogen peroxide, at a concentration greater than 10 wt %, autoacceleration of the

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decomposition reaction represents the greatest risk. As observed experimentally, the time to reach the maximum rate is well under an hour, often less than 10 min, and the energy evolution rate is between 300 and 1500 W/kg. Under the conditions where the temperature has begun to increase rapidly, it is unlikely that any control system will stop the reaction, and systems must be designed to limit the consequences, for example, properly sized rupture disks and piping. Even with pressure relief systems, rapid autoacceleration could lead to supersonic flow and a corresponding shock wave.

Another consideration in doing a risk assessment is the extent of damage if control is lost. When one considers the previous explosions involving accumulation of high-strength hydrogen peroxide in pumps, both events resulted in shutdown of a significant portion of the mill site and required extensive repairs. While these events did not result in fatalities, there was a high potential for loss of life. An international standard IEC 61511[28] provides guidance on the level of redundancy and independence of control systems. The maximum SIL described is level 4, which should be used for processes that present the most hazard and have severe consequences. Under this standard, open or sufficiently vented, >10 wt % hydrogen peroxide processes should have SIL 4 level controls.

If a pulp bleaching facility wants to implement the recommendation that they switch from feeding 50−10 wt % hydrogen peroxide into their mixer, there will have to be several process modifications. For example, pulp dilution will have to be adjusted to account for the increased amount of water coming in with a hydrogen peroxide solution. Mills will likely continue to store hydrogen peroxide at 50% and add inline dilution. As with any dilution of hydrogen peroxide, water with low levels of contaminants, especially transition-metal ions, will be critical. While the dilution unit operation will still present hazards and its control system will require SIL 4, the rest of the bleaching process will become inherently safe. If the dilution occurs near the storage tank, one will gain the added safety of internal mill piping containing lower concentrations of hydrogen peroxide.

Following the same risk assessment steps, one reaches a conclusion that closed, or inadequately vented, systems should never be considered safe, even for hydrogen peroxide concentrations below 10%. Depending on the physical situation, very large pressure pulses can be expected. When Wu and Qian[2] ran experiments with 30% hydrogen peroxide in a half-filled closed reactor, the pressure peaked at 16 MPa, 2300 psig, over the course of about 10 s. This pressure pulse was due to both the rapid increase in temperature and generation of oxygen gas during the decomposition reaction. Because closed systems are never safe, careful consideration must be given to process designs that can inadvertently become closed. For example, the bridging of pulp in a pipe can result in a blockage, and if there is no pressure relief, the system can become closed and thus explode.

Transition-metal catalysis of hydrogen peroxide decomposition is widely known and has been implicated in several accidents.[3] It is practically impossible to conduct experiments with hydrogen peroxide without having to consider the impact of transition-metal ions,[29] and during the development of new experiments or process with hydrogen peroxide, consideration should be given to the concentration of all transition metals. In our previous study,[5] we have highlighted the importance of iron contamination of sodium hydroxide solutions. In this study, we have chosen to largely keep the iron concentration in the sodium hydroxide solution constant at 0.5 ppm. Even at this low concentration, the impact is dramatic, see Figure 4. The value of 0.5 ppm represents an estimate of the iron concentration in typical membrane-grade sodium hydroxide, which is often marketed as higher purity, low salt. The standard-grade sodium hydroxide is made with a less selective diaphragm process, which often results in an order of magnitude greater iron concentration, 5−10 ppm. While negotiated prices for bulk sodium hydroxide vary, there is often a significant price differential between diaphragm- and membrane-grade sodium hydroxide, and often diaphragm grade is $20−40/ton cheaper. Mill operators should be aware that choosing a lower grade of sodium hydroxide to save money may result in a significantly increased hazard level.

CONCLUSIONS

Using fundamental chemical engineering equations, a model for the decomposition of hydrogen peroxide under alkaline conditions was developed and validated. The RMS temperature difference between the model and experiments was 0.13 °C. This model includes an estimate of the mixture heat capacity, rate constants for both alkaline and iron-catalyzed decomposition of hydrogen peroxide, and heat loss associated with evaporation.

The model was exercised over a range of compositions and temperatures to calculate the parameters required for a safety analysis. Following a standard practice, criticality and SIL of the controls were determined. For bleaching processes that use hydrogen peroxide at a concentration less than 10 wt %, one can consider that the process is inherently safe because the thermal mass of the system is sufficient to prevent reaching an autoacceleration condition. Processes that use hydrogen peroxide at greater than 10 wt %. can autoaccelerate, and thus, the criticality class is 4 and the controls require SIL 4. Applying the same analysis to closed systems indicates that they are never safe, even if the hydrogen peroxide concentration is less than 10 wt %.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.2c01868.

Listing of the Python code implementing the model, fitting, and plotting (TXT)

Data file with all of the temperature versus time data (TXT)

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Notes

The authors declare no competing financial interest.

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