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Modeling and Estimation of Reaction Constants in Hydrogen Peroxide Deterioration Reactions

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Abstract—In this paper, a new model in augmented state space allowing for faster prediction of hydrogen peroxide decay rates is proposed. This information is important for the development of new hydrogen peroxide solutions used to fight pathogens and harmful germs. The well-known Kalman filter and the unscented Kalman filter are applied on developed mathematical models and experimental measurements. The results are compared and discussed.

Keywords—Hydrogen peroxide; unscented Kalman filter; interacting multiple models

I. INTRODUCTION

Virox Technologies Inc. (Oakville, Ontario) specializes in the development of innovative cleaning and disinfection technologies based on hydrogen peroxide as the active ingredient. Hydrogen peroxide is an optimal ingredient for use in disinfectant formulations as it has a wide spectrum of antimicrobial efficacy, has a highly preferred environmental profile, and does not leave toxic residues on surfaces upon application (i.e., it breaks down to water and oxygen). More specifically, Virox Technologies Inc. is an industry leader in innovating peroxide based antimicrobial formulations wherein very low concentrations of hydrogen peroxide (less than 1%) is synergistically made to be highly effective against pathogenic organisms. This selective acceleration of hydrogen peroxide's activity against pathogens has been possible by blending hydrogen peroxide with specific types and amounts of readily available and safe inert ingredients; such as anionic surfactants, cyclic carboxylic acids, and more. The innovative discoveries on synergistic mixtures of hydrogen peroxide at low concentrations with the select inert additives has led to development of the multi-patented accelerated hydrogen peroxide (AHP) technology platform. Today, products based on the AHP technology platform are found in over 60 countries worldwide, and in about 75% of Canadian healthcare institutions.

Experiments performed at Virox have shown that collecting statistically significant data regarding hydrogen peroxide decay requires weeks of incubation time. The need of an accelerated degradation method is required to speed up the determination of hydrogen peroxide lifetime. This paper suggests a hypothetical setup using estimation strategies that predict two parameters: temperature variation, and hydrogen peroxide concentration.

State and parameter estimation theory is an important field in mechanical and electrical engineering. The strategies are used to predict, estimate, or smooth out important system state and parameters [1, 2]. The Kalman filter (KF) is the most popular estimation strategy, and yields a statistically optimal solution to the linear estimation problem [3]. The goal of the KF is to minimize the state error covariance, which is a measure of the estimation accuracy and is defined as the expectation of the state error squared [4]. The state error is defined as the difference between the true state value and the estimation state value. Although the KF yields a solution for linear estimation problems, it is based on a few strict assumptions: the system and measurement models must be known, the noise distribution is Gaussian, and the behavior is linear [5, 6]. If any of these assumptions are not held by the actual system, then the KF may yield inaccurate or unstable estimation results [7]. A popular nonlinear form of the Kalman filter is the unscented Kalman filter (UKF). It utilizes statistics to approximate the nonlinear probability density function (PDF) [8].

For the experiments performed in this paper, the following assumptions have been made: (1) reactions are first order only. In the event that this is not the case, one can still consider reactions as pseudo-first order but with a different reaction constant $\boldsymbol{k_{obs}(t)}$ [9]; and, (2) the loss of hydrogen peroxide is independent on the concentration when the concentration is low. This applies to the experiments in this paper due to the fact that hydrogen peroxide concentrations were relatively low, ranging between 0.5% to 2% of total solution weight. The experimental data is described in Section 2, the methods and analysis are described in Section 3, the results are found in Section 4, and the papers is then concluded.

II. EXPERIMENTAL DATA

Experimental data was obtained within the facilities at Virox and averaged in order to determine initial reaction constant and variances that needed to be fed into matrix R, the measurement noise covariance. A summary of data is available in Tables I through III.

Based on this data, it is sufficient to determine the reaction constant k, activation energy E_a (also known as the enthalpy of decomposition), and the initial parameter A_0 which come into the Arhenius equation in (1). In (1), R is the universal gas constant and T is the temperature.

$$k[H_2O_2] = A_0\exp(-Ea/RT) \tag{1}$$

In order to determine ***k***, one linearly fits the natural log of peroxide loss over time via following relationship:

$$\ln[C(t)/C_0] = -k[H_2O_2]t \tag{2}$$

where C(t) and C_0 are the concentrations of the current and initial time steps respectively. Analogously, one fits reciprocal temperature to natural log of k to determine $\boldsymbol{E_a}$ and $\boldsymbol{A_0}$:

$$(-Ea/RT) + \ln(A_0) = \ln(k(T)) \tag{3}$$

Plots of the curve fitting described by (2) and (3) are shown in Fig. 1 and 2.

TABLE I. PERCENT LOSS OF H_2O_2 AT 50°C

Time (Hr)	pH = 2		pH = 3		pH = 4		pH = 5	
	% Loss	Error	% Loss	Error	% Loss	Error	% Loss	Error
120	0.16	0.27	0.00	0.00	0.02	0.03	0.00	0.00
240	1.43	0.55	0.00	0.00	0.49	0.47	0.06	0.10
360	2.92	1.06	0.06	0.08	0.47	0.41	0.21	0.27

TABLE II. PERCENT LOSS OF H_2O_2 AT 54°C

Time (Hr)	pH = 2		pH = 3		pH = 4		pH = 5	
	% Loss	Error	% Loss	Error	% Loss	Error	% Loss	Error
120	1.37	0.70	0.07	0.07	0.03	0.04	0.00	0.00
240	2.41	0.85	0.35	0.60	0.51	0.51	0.04	0.03
360	2.97	0.95	0.21	0.36	0.24	0.41	0.00	0.00

TABLE III. PERCENT LOSS OF H_2O_2 AT 70°C

Time (Hr)	pH = 2		pH = 3		pH = 4		pH = 5	
	% Loss	Error	% Loss	Error	% Loss	Error	% Loss	Error
120	1.680	1.94	0.03	0.06	0.03	0.05	0.00	0.00
240	7.85	1.29	0.07	0.07	0.00	0.00	0.12	0.21
360	10.98	1.05	0.30	0.52	0.71	0.72	0.04	0.07

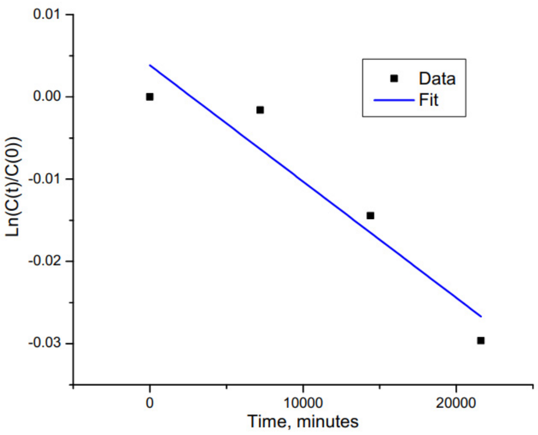

Figure 1. Linear fit of (2).

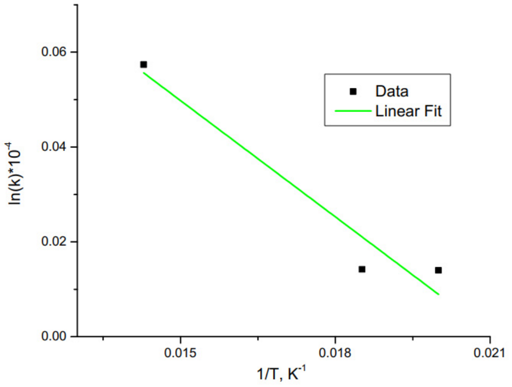

Figure 2. Linear fit of (3).

Both of these fits from Fig. 1 and 2 can provide all required ingredients for the determination of k. The constants have been determined as follows:

$$E_a = 70 \text{ kJ} \times \text{mol}^{-1}$$
$$A_0 = 0.4 \times 10^{5.8} \text{ min}^{-1}$$
$$k = 1.45 \times 10^{-6} \text{ min}^{-1} \text{ at } 50°\text{C}$$

The obtained values are within reasonable agreement with results published elsewhere for aqueous solutions, keeping in mind the pH levels in this study [10]. Additionally, analysis of k constants was performed on various pH levels. Results are depicted in Fig. 3. As there are only 4 points, there is no clear relationship between k and pH. Therefore, it will be omitted in calculations.

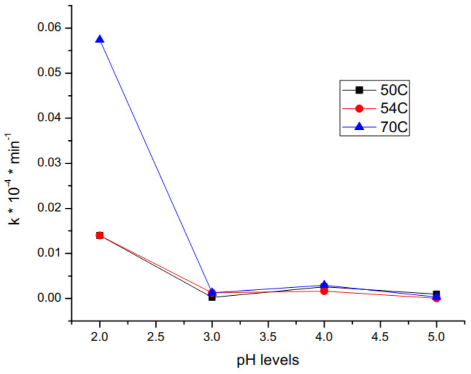

Figure 3. K at various pH Levels.

III. METHODS AND ANALYSIS

A. Linear System of Equations

The augmented state space system is based on three variables, ***c*** - concentration, ***T*** - temperature, and ***k*** - reaction rate constant. The discretized augmented state space system is written as:

$$\begin{bmatrix} c_{i+1} \\ T_{i+1} \\ k_{i+1} \end{bmatrix} = \begin{bmatrix} -k_i\Delta t + 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} c_i \\ T_i \\ k_i \end{bmatrix}, \tag{4}$$

where Δt is sampling time (200 minutes). Initial conditions for all simulations are shown in (5).

$$\begin{bmatrix} c_0 \\ T_0 \\ k_0 \end{bmatrix} = \begin{bmatrix} 0.1615 \;\; \mathrm{M} \\ 323.50 \;\; \mathrm{K} \\ 1.45 \times 10^{-6} \;\; \mathrm{min}^{-1} \end{bmatrix} \tag{5}$$

B. Determination of Q and R matrices

In most cases, only ***c*** and ***T*** are measurable during experiments. Thus, H, or measurement matrix, is written as:

$$H = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \tag{6}$$

Additionally, the noise covariance matrices Q (system noise) and R (measurement noise) are required to run any type of Kalman filter. The determination of R is straightforward and it is obtained through experimental setup. For this study, it is determined to be:

$$R = \begin{bmatrix} 5 \times 10^{-8} & 0 \\ 0 & 0.01 \end{bmatrix} \tag{7}$$

The determination of the Q matrix is usually the trickiest part of Kalman filtering. Matrix elements of Q are treated as tunable parameters which are determined based on the uncertainties that may arise in a system. With this experiment, these uncertainties might be temperature and humidity variations. Additionally, for the augmented state space system, matters become more complicated due to the fact that the augmented part of the system, shown below:

$$\begin{bmatrix} T_{i+1} \\ k_{i+1} \end{bmatrix} = \begin{bmatrix} T_i + w_T(i) \\ k_i + w_k(i) \end{bmatrix} \tag{8}$$

This becomes a Wiener process with unbounded variance shown in (9). One solution to this problem is to set variances w_T, w_K to zero. However, doing so would change the controllability of the system.

$$\lim_{i\to\infty} \mathrm{Var}(T, k) = \infty \tag{9}$$

There is another way, however, to keep variances nonzero while having bounded covariances of augmented state variables. This is described in [2], and the procedure is as follows:

- Choose matrix elements of Q to be a few percent of estimated values
- Run simulations for true and Kalman estimated systems
- Calculate variances of simulated variables
- Adjust matrix elements of Q such that (10) is satisfied

$$\mathrm{Var}(x) = \lim_{i\to\infty} \mathrm{P}_i(x) \tag{10}$$

The procedure from [3] was adopted and the resulting Q matrix was determined to be:

$$Q = \begin{bmatrix} 10^{-9} & 0 & 0 \\ 0 & 2 \times 10^{-8} & 0 \\ 0 & 0 & 10^{-16} \end{bmatrix} \tag{11}$$

C. System Setup and Kalman Estimators

The estimators used in this study were the Kalman filter (KF), unscented Kalman filter (UKF), and the interacting multiple model (IMM) setup based on the KF and the UKF. For the IMM algorithm, (12) was used as the probability transition matrix:

$$R = \begin{bmatrix} 0.95 & 0.05 \\ 0.05 & 0.95 \end{bmatrix} \tag{12}$$

Temperature profiles were treated as unknown parameters fed into the Kalman estimators. The main objective was to assess the accuracy of predicted reaction rate constants compared to their true counterparts.

IV. RESULTS

A. *Profiles with Rising Temperatures*

Rising temperature profiles were simulated through raising the temperature by a certain amount at $pH = 2$ as demonstrated in Fig. 4, Fig. 5, and Fig. 6. The three state variables (Peroxide concentration, temperature, and k-constant) are shown in each of these figures, along with the KF, UKF, and IMM results. The probabilities (Mu) of the IMM system being in the KF or UKF mode are also shown.

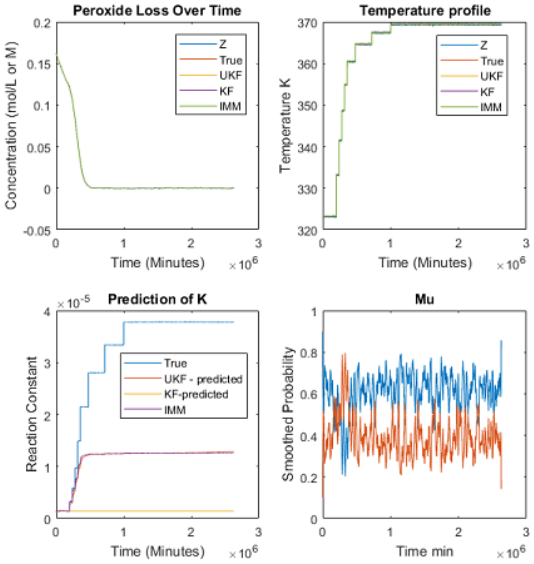

Figure 4. Temperature profile with a 50°C change.

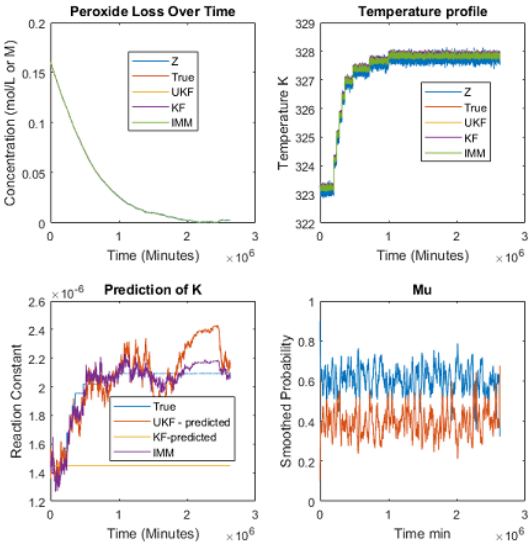

Figure 5. Temperature profile with a 5°C change, late onset.

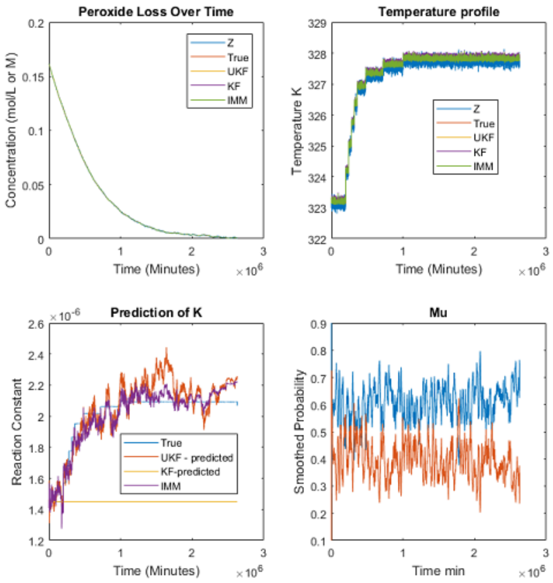

Figure 6. Temperature profile with a 5°C change, early onset.

It is interesting to note that in the case of large temperature change, neither one of the Kalman estimators provided correct values of k. At lower changes in temperature and based on the root mean square errors (RMSE) seen in Tables IV and V, one can see that the IMM and the UKF are similar in accuracy. The plain KF is unable to estimate the non-linear k constant of the system.

TABLE IV. RMSE'S FOR TEMPERATURE PROFILE WITH A 5°C CHANGE, LATE ONSET

System States	**Estimator RSME**		
	KF	**UKF**	**IMM**
Concentration (M)	8.64662×10^{-5}	8.60678×10^{-5}	8.41062×10^{-5}
Temperature (K)	5.25555×10^{-1}	1.41209×10^{-1}	7.67782×10^{-2}
K Constant (min^{-1})	5.85417×10^{-7}	1.60082×10^{-7}	6.5447×10^{-8}

TABLE V. RMSE'S FOR TEMPERATURE PROFILE WITH A 5°C CHANGE, EARLY ONSET

System States	**Estimator RSME**		
	KF	**UKF**	**IMM**
Concentration (M)	8.14059×10^{-5}	8.15825×10^{-5}	7.98528×10^{-5}
Temperature (K)	5.26052×10^{-1}	1.401×10^{-1}	7.6568×10^{-2}
K Constant (min^{-1})	5.84784×10^{-7}	1.09314×10^{-7}	6.8593×10^{-8}

B. *Profiles with Random Temperature Changes*

Experimental setup remains the same as described in the preceding section, but here the temperature profiles have random temperature variations to simulate hydrogen peroxide products being used and stored under real world conditions.

The simulation results are shown in Fig. 7 through Fig. 9 and Tables VI through VIII.

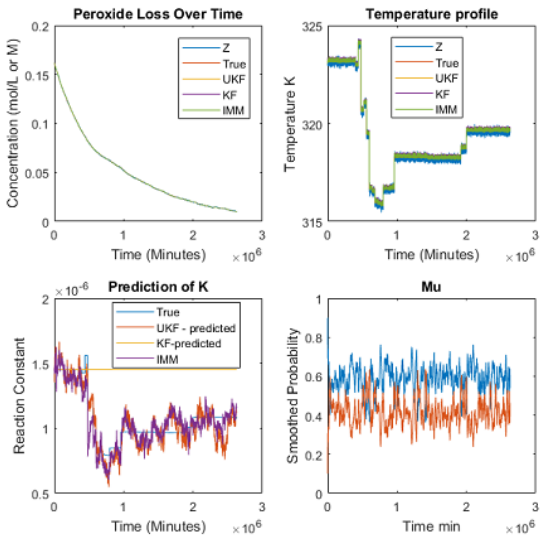

Figure 7. First profile with random temperature variation.

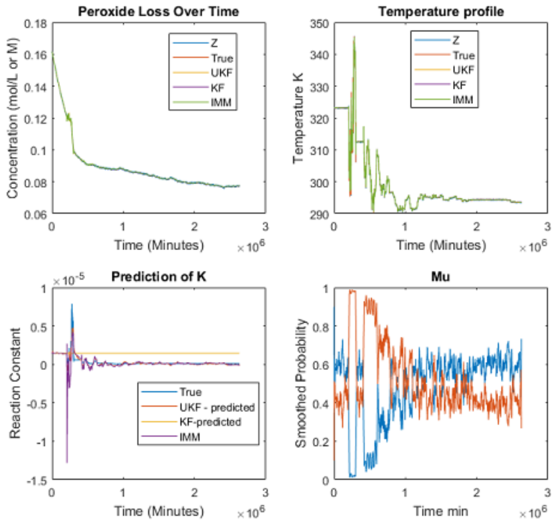

Figure 8. Second profile with random temperature variation.

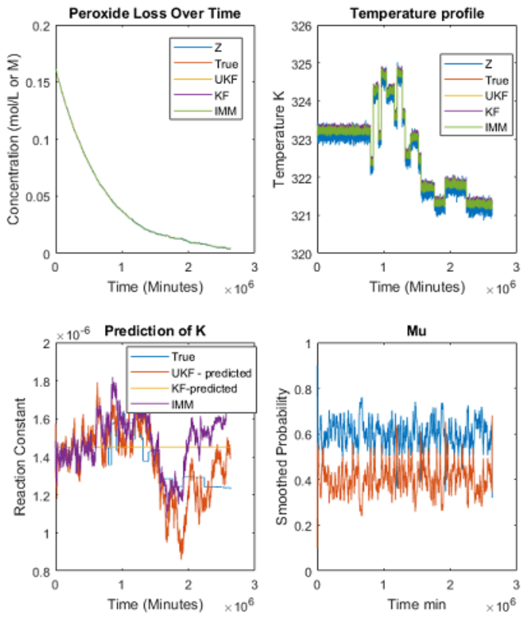

Figure 9. Third profile with random temperature variation.

TABLE VI. RMSE'S FOR FIRST PROFILE WITH RANDOM TEMPERATURE VARIATION

System States	**Estimator RSME**		
	KF	**UKF**	**IMM**
Concentration (M)	8.60051×10^{-5}	8.54607×10^{-5}	8.3524×10^{-5}
Temperature (K)	1.02656	1.51515×10^{-1}	9.73733×10^{-2}
K Constant (min^{-1})	1.34067×10^{-7}	1.29145×10^{-7}	1.71801×10^{-7}

TABLE VII. RMSE'S FOR SECOND PROFILE WITH RANDOM TEMPERATURE VARIATION

System States	**Estimator RSME**		
	KF	**UKF**	**IMM**
Concentration (M)	1.74623×10^{-4}	2.27619×10^{-4}	2.25101×10^{-4}
Temperature (K)	4.55449	6.321×10^{-1}	6.21528×10^{-1}
K Constant (min^{-1})	1.29936×10^{-6}	2.91613×10^{-7}	6.26771×10^{-7}

TABLE VIII. RMSE'S FOR THIRD PROFILE WITH RANDOM TEMPERATURE VARIATION

System States	**Estimator RSME**		
	KF	**UKF**	**IMM**
Concentration (M)	8.13347×10^{-5}	8.34285×10^{-5}	8.16195×10^{-5}
Temperature (K)	4.56238×10^{-1}	1.47175×10^{-1}	8.8286×10^{-2}
K Constant (min^{-1})	1.34067×10^{-7}	1.29145×10^{-7}	1.71801×10^{-7}

Based on Fig. 7 through Fig. 9 and Tables VI through VIII, one can see that the general trend is preserved. The UKF and IMM do the best job at predicting the reaction constant k, in terms of state estimation error. Additionally, the probability of switching between KF and UKF modes are more pronounced during large temperature variations. This indicates the robustness of IMM predictions with respect to random temperature spikes.

V. CONCLUSION

This paper proposes a new augmented state space model for faster prediction of hydrogen peroxide decay under any user-defined temperature profile. It was shown that the best state estimation accuracy was achieved by the UKF and IMM methods. Additionally, it was shown that for the IMM and UKF to have the best accuracy, low temperature changes and shorter durations of particular temperature variations are required. In terms of future work, more temperature profiles will be tested, and the pH level will be incorporated into the model. As the team was unable to find equations that relate the pH level to the rate of reaction, the effects of pH level would have to be incorporated through experimental data. The team will utilize a small set of experimental data with combined estimation and deep learning algorithms to create a more comprehensive model in the future.

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REFERENCES

[1] B. D. O. Anderson and J. B. Moore, Optimal Filtering, Englewood Cliffs, NJ: Prentice-Hall, 1979.

[2] Y. Bar-Shalom, X. Rong Li and T. Kirubarajan, Estimation with Applications to Tracking and Navigation, New York: John Wiley and Sons, Inc., 2001.

[3] S. A. Gadsden, "Smooth Variable Structure Filtering: Theory and Applications," Ph.D. Thesis, McMaster University, Hamilton, Ontario, 2011.

[4] M. S. Grewal and A. P. Andrews, Kalman Filtering: Theory and Practice Using MATLAB, 3 ed., New York: John Wiley and Sons, Inc., 2008.

[5] S. A. Gadsden and S. R. Habibi, "A New Form of the Smooth Variable Structure Filter with a Covariance Derivation," in *IEEE Conference on Decision and Control*, Atlanta, Georgia, 2010.

[6] R. E. Kalman, "A New Approach to Linear Filtering and Prediction Problems," *Journal of Basic Engineering, Transactions of ASME,* vol. 82, pp. 35-45, 1960.

[7] D. Simon, Optimal State Estimation: Kalman, H-Infinity, and Nonlinear Approaches, Wiley-Interscience, 2006.

[8] S. A. Gadsden and A. S. Lee, "Advances of the Smooth Variable Structure Filter: Square-Root and Two-Pass Formulations," *Journal of Applied Remote Sensing,* vol. 11, no. 1, pp. 1-19, 2017.

[9] S. S. Lin and M. Gurol, "Catalytic Decomposition of Hydrogen Peroxide on Iron Oxide: Kinetics, Mechanism, and Implications," *Environmental Science and Technology,* vol. 32, pp. 1417-1423, 1998.

[10] J. Tajagi and K. Ishigure, "Thermal Decomposition of Hydrogen Peroxide and Its Effect on Reactor Water Monitoring of Boiling Water Reactors," *Nuclear Science and Engineering,* vol. 89, pp. 177-186, 1985.

[11] H. H. Afshari, S. A. Gadsden and S. R. Habibi, "Gaussian Filters for Parameter and State Estimation: A General Review and Recent Trends," *Signal Processing,* vol. 135, pp. 218-238, 2017.