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Sensor Technology using Fluorescent Dyes

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Sensor Technology using Fluorescent Dyes

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Introduction

The ChemTreat sponsored senior design project, involves the utilization of fluorescent dye technology engineered as a real-time leak detection system for recovery boilers in industrial plants. Fluorescent dyes, such as pyrenetetrasulfonic acid (PTSA), are detectable at very low concentration on the magnitude of parts per billion, making them ideal candidates for applications in fluid mechanics.

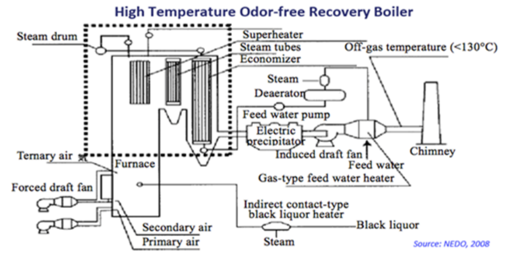


Figure 1. Process flow diagram for High Temperature Recovery Boiler.

Abstract

Reaction kinetics were determined for PTSA from batch reactions, which were carried out in microwave reactors. It was established that PTSA decomposed on a 1st order reaction rate, and corresponding mathematical models were established using mass and energy balances. MATLAB simulations are provided and compared with actual experimental data conducted in a CSTR to demonstrate the accuracy of the mathematical model. The leak detection system is based on steady-state conditions using the PTSA mass balance model as a reference point for any changes that might occur in the system.

Methods

- Dye Reaction Kinetics
  - Batch Reactions
  - Biotage Microwave
  - CEM Microwave
- Boiler Simulations
  - CSTR
  - MATLAB

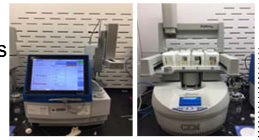


Figure 2. Biotage (left) and CEM (right)

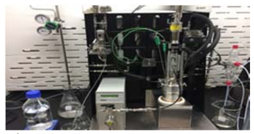


Figure 3. CSTR

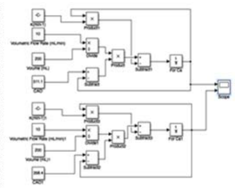


Figure 4. MATLAB Simulink block diagram.

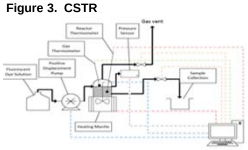


Figure 5. P&ID for CSTR.

Mathematical Model

(Eq.1) $\frac{dN_a}{dt} = F_{a0} - F_a + r_a V$

(Eq.2) $\frac{dC_a}{dt} = \frac{\dot{v}}{V}(C_{a0} - C_a) - kC_a$

(Eq.3) $C_a = \frac{\beta}{\alpha}(1 - e^{-\alpha t})$

$where\ \alpha = \frac{1}{\tau} + k, \quad \beta = \frac{1}{\tau}C_{a0}, \quad and\ \tau = \frac{V}{\dot{V}}$

(Eq.4) $C_a = e^{-\alpha t}\left(C_{a0} - \frac{\beta}{\alpha}\right) + \frac{\beta}{\alpha}$

(Eq.5) $k_n = Ae^{\left(E_a/_{RT}\right)}$

Assumptions:
- Well-mixed system
- Volume and volumetric flow rate are constant
- 1st Order homogeneous rxn
- Steady-State
- Density is constant
- Dilute solution
- Constant T and P

- Mass balance for CSTR
- Eq.3 Boundary conditions: C_a=0 at t=0
- Eq.4 Initial conditions: t=0, C_a=C_{ao}
- Eq.5 Arrhenius Equation

Results

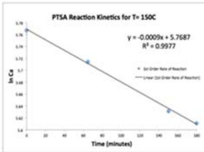


Figure 6. Batch reaction results for decomposition of PTSA at T= 150°C.

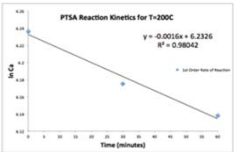
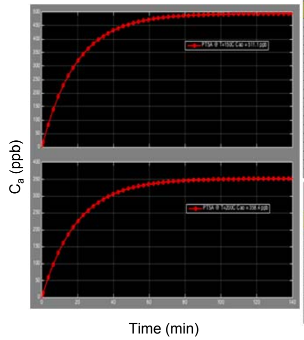


Figure 7. Batch reaction results for decomposition of PTSA at T= 200°C.

MATLAB Simulation for CSTR



Cao = 511.1 ppb V=200 mL Flow rate = 10 mL/min @ T= 150°C	
Time (min)	Ca (ppb)
22	357.20
25	367.00
30	399.80
35	415.30
40	426.70
45	436.20
50	441.60
55	453.30
57	458.90
60	458.40
65	460.40
70	465.50
75	456.10
80	455.30
85	456.10
90	464.70
95	465.50
100	467.90

Cao = 358.4 ppb V=200 mL Flow rate = 10 mL/min @ T= 200°C	
Time (min)	Ca (ppb)
60	310.00
65	302.00
70	304.00
75	319.00
80	319.00
85	318.50
90	318.90
95	320.20
100	323.60
105	326.00

Figure 8. Using the rate constants k(min^{-1}) found from the slope of the line in Figure 6 and 7 to simulate the change in concentration of PTSA over time (left). Experimental data collected from CSTR trials (right).

Future Progress

- Further experimentation of PTSA at higher temperatures and pressures
- Search additional dyes for testing
- Design apparatus for boiler leak simulation
- Find compatible dye pairs for dual dye leak detection system

Financial and Environmental Analysis

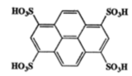


Figure 9. Chemical Structure of PTSA.

Figure 10. Chart for causes of critical leaks in recovery boilers.

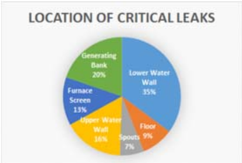


Figure 11. Chart for location of leaks in recovery boilers.

- Improved leak detection methods reduce losses associated with an emergency shutdown
- This technology could save the industry an estimated $1.1 million in losses per day per mill to avoid an emergency shutdown [1]
- Data regarding the ecotoxicological properties of fluorescent tracers are scarce [2]
- Current data shows that both dyes are mostly environmentally benign
- Decomposition products of PTSA include Carbon Monoxide (CO), Carbon Dioxide (CO_2), Sulfur Oxides [3]

References

- Acros Organics Safety Data Sheet. 1,3,6,8-Pyrenetetrasulfonic acid tetrasodium salt. Revision Date: 10-Feb-2015.[3]
- Gombert P., Biaudet H., de Seze R., Pandard P. and Carré J., 2017. Toxicity of fluorescent tracers and their degradation byproducts. International Journal of Speleology, 46 (1), 23-31.[2]
- Smith, Brent R., Rice, R.W., Ince, Peter J. 2003. Pulp Capacity in the United States, 2000. Gen. Tech. Rep. FPL-GTR-139. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, 23 p.[1]

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