Oxidative Treatment of Industrial Wastewater: Development of Novel catalysts and technology Evaluation

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Motivation for Research

Pulp and paper mills and distillery units use large quantities of fresh water.

As a result, enormous amounts of wastewater are produced, containing organic and inorganic compounds

Most of these compounds are not easily treated biologically (i.e. lignin) and are highly toxic to the environment

The resulting wastewater requires oxidative degradation before biological treatment.

Development of efficient catalyst which operates at modest conditions is critical

The focus of this project is to develop more advanced and cost effective technologies for this process

Scope of Project

Catalyst Development

- Develop a catalyst that catalyzes the oxidation of ferulic acid (model lignin compound) in the presence of air at mild temperatures and pressures

Kinetic Modeling

- Develop a kinetic model that sufficiently details the behavior of the system.

Reactor/Process Modeling

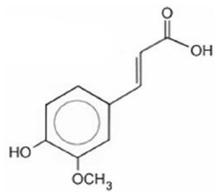
- Develop a reactor model to describe the behavior of the process on the industrial scale in order to estimate an overall mass balance, energy requirements, and the economics of the process.

Catalyst Development and Experimental Work

What was studied?

- A model lignin compound was chosen as ferulic acid (Figure 1)
- Ferulic acid was reacted in the presence of air with (Catalytic Wet Oxidation, CWO) and without (Wet Oxidation, WO) the developed catalyst (CuO/CeO_2) at various temperatures.
- The reactions were carried out in a high pressure stainless steel batch reactor with an impeller and internal heating/cooling coils, seen in Figure 2.
- A mixing study was performed to ensure mass transfer limitations of oxygen were not an issue
- A temperature study was performed to see the effect of temperature on the WO and CWO system.
- Total organic carbon (TOC) data was collected over the time span of each experiment

Figure 1: Molecular Structure of Ferulic acid ($C_{10}H_{10}O_4$)



A

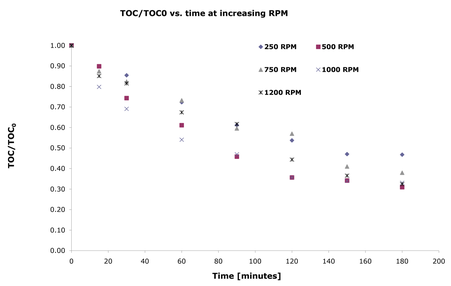
B

Figure 2: High pressure stainless steel batch setup. A) Fully assembled setup B) Heating/cooling coils with impeller (surrounded by coils)

Catalyst Development and Experimental Work (continued)

Mixing and temperature studies:

- TOC versus time data was collected throughout each experiment held at constant RPM from 250-1200 RPM (Figure 3A)
- TOC versus time data was collected throughout each experiment held at constant temperatures from 363K-433K at constant pressure 0.8 MPa(Figure 3)



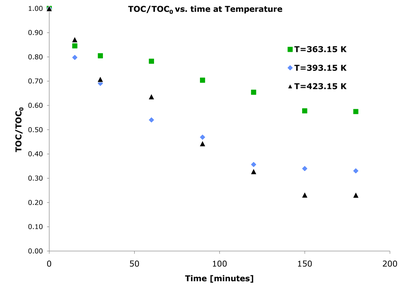


Figure 3: A) TOC/TOC_0 versus time results for increasing RPM (left) B) TOC/TOC_0 versus time results for increasing reactor vessel temperature (right). Both are for simultaneous catalytic and non-catalytic wet oxidation of ferulic acid in the presence of air.

Key results of experimental work

- The catalyst reduces ferulic acid in the reactor vessel to around 50-75% of the original TOC at temperatures of 90-150C and 1 MPa pressure.
- The reaction can be assumed to have minimal mass transfer effects at RPM around 1000 due to no further conversion of TOC close to or after 1000 RPM
- The overall reactions show an increase in TOC conversion with increased temperature

Kinetic Modeling

What is involved in kinetic Modeling?

1) Make assumptions that simplify complex chemistry; 2) derive rate equations to describe behavior of assumed chemistry; and 3) determine the kinetic parameters from gathered experimental data.

3 main kinetic models investigated

Simple TOC based Model: All organic species are approximated by a single parameter (TOC)

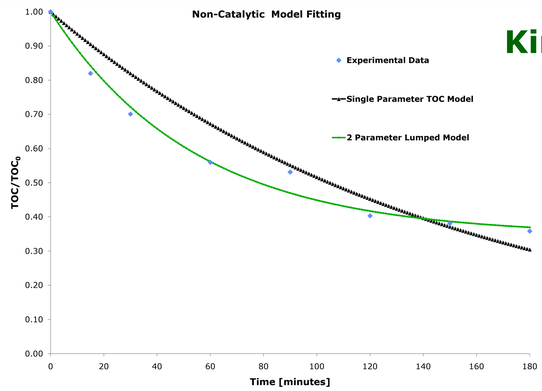
2 Parameter Lumped Model*: Only intermediates are lumped together (non-catalytic)

4 parameter Lumped Model*: Only intermediates are lumped together (both catalytic/non-catlytic)

***Based on similar work by Qinglin Zhang and Karl T. Chuang. Lumped kinetic model for catalytic wet oxidation of organic compounds in industrial wastewater. AIChE Journal, 45(1):145-150, 1999.**

Overall Chemical Reactions		Rate Equations
$A+O_2 \xrightarrow{k_1,non-catalytic} CO_2+H_2O$ $A+O_2 \xrightarrow{k_2,catalytic} CO_2+H_2O$	Simple TOC Based Model	$-r_{A,non-cat}=k_1[TOC][O_2]$ $-r_{A,cat}=k_1[TOC][O_2]+k_2[cat][TOC][O_2]$
$\underline{Non-Catalytic}$ $A+10.5O_2 \xrightarrow{k_1} 10CO_2+5H_2O$ $A+\nu_{(2,2)}O_2 \xrightarrow{k_2} \nu_{(2,3)}B+\nu_{(2,4)}H_2O$	2 Parameter lumped Model Non-catalytic	$-r_A=k_1[A][O_2]^{n_1}+k_2[A][O_2]^{n_2}$ $r_B=k_2[A][O_2]^{n_2}$ $[TOC]=[A]+[B]$ $[CO_2]=[A]_0-[TOC]$
$\underline{Non-Catalytic}$ $A+10.5O_2 \xrightarrow{k_1} 10CO_2+5H_2O$ $A+\nu_{(2,2)}O_2 \xrightarrow{k_2} \nu_{(2,3)}B+\nu_{(2,4)}H_2O$ $\underline{Catalytic}$ $A+10.5O_2 \xrightarrow{k_3} 10CO_2+5H_2O$ $A+\nu_{(4,2)}O_2 \xrightarrow{k_4} \nu_{(4,3)}B+\nu_{(4,4)}H_2O$	4 Parameter lumped Model Simultaneous Catalytic/Non-Catalytic	$-r_A=k_1[A][O_2]^{n_1}+k_2[A][O_2]^{n_2}$ $+k_3[cat][A][O_2]^{n_3}+k_4[cat][A][O_2]^{n_4}$ $r_B=k_2[A][O_2]^{n_2}+k_4[cat][A][O_2]^{n_4}$ $[TOC]=[A]+[B]$ $[CO_2]=[A]_0-[TOC]$

Kinetic Modeling (continued)



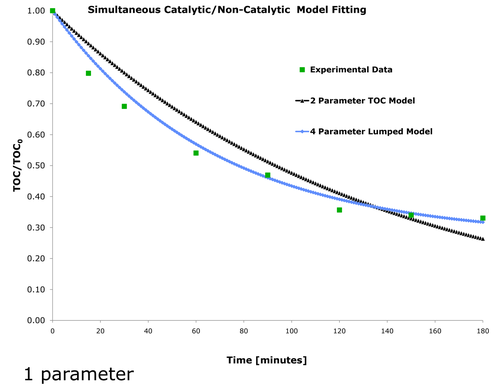


Figure 4: TOC/TOC_0 versus time results for both non-catalytic (above) and simultaneous catalytic/non-catalytic (right) reactions are fit to equations below.

Assumption: no mass transfer limitations, O2 concentration is equal to the solubility and is maintained at a constant value

$$\frac{TOC}{TOC_0}=\exp(-(k_1[O_2])t)$$ 1 parameter Simple TOC

$$\frac{TOC}{TOC_0}=\exp(-(k_1[O_2]+k_2[O_2][cat])t)$$ 2 parameter Simple TOC

$$\frac{TOC}{TOC_0}=\frac{k_2'}{k_1'+k_2'}+\frac{k_1'}{k_1'+k_2'}\exp(-(k_1'+k_2')t)$$ 2 Parameter Lumped Model

$$\frac{TOC}{TOC_0}=\frac{k_2'+k_4'}{k_1'+k_2'+k_3'+k_4'}\left(-\exp(-(k_1'+k_2'+k_3'+k_4')t)\right)+\exp(-(k_1'+k_2'+k_3'+k_4')t)$$ 4 Parameter Lumped Model

Key results of kinetic modeling work

- The lumped kinetic models showed better agreement than a simple TOC based model in Figure 4.
- Fitting k-values for the 4 parameter lumped kinetic model were more difficult due to oversimplification of k-values (i.e. lumped [cat] terms inside k' values)
- The lumped models did not show asymptotic behavior with data, which is problematic when describing behavior at higher time values.

Conclusions

What conclusions can be drawn from this work?

- The TOC vs. time data was sufficient for simple kinetic models describing the behavior of the system.
- The lumped kinetic models fit experimental data better than the simple TOC model (both single and 2 parameter).
- More experimental work addressing catalyst loading will enhance results for 4 parameter lumped kinetic model.
- Reactor modeling is currently being performed in OpenFOAM and coupled with SuperPro Designer to provide economic analysis for the overall investigation.
- The entire process of judging efficacy of a catalyst not only depends on laboratory performance, but a full quantitative evaluation on the reactor and process scale through reactor and process modeling.
- See our full MAGEEP report for more details