Employing Least Squares and Piecewise Cubic Hermite Interpolating Polynomial Fitting to Analyze In-Situ Raman Spectroscopy Data

Elizabeth Rasmussen
Final Presentation
ME 535 – Spring 2018
Introduction
Motivation
Methods
Results
- Automatic Background Subtraction
- Concentration Analysis
Conclusions and Future Work
Introduction: Supercritical Reactors + Raman Spectroscopy

• A research project funded by the US Defense Threat Reduction Agency (DTRA) in the mechanical engineering department is developing a new means of neutralizing chemical warfare agents (CWA) using a single-step, continuous supercritical water hydrolysis (CScWH) reactor platform.

• The fast decomposition of these highly stable biomass compounds suggests that CWA molecules can be destroyed via supercritical hydrolysis (1).

Introduction: Supercritical Reactors + Raman Spectroscopy

• The ability to instantaneously collect and analyze a substance’s composition is of great value in defensive military applications such as verifying the neutralization of chemical warfare agents.

• *In-situ* Raman spectroscopy significantly reduces experimental uncertainty and experimentation time, while allowing for the accurate identification of decomposition products [1,2].

![Raman spectra](image)

**Figure 2.** Raman spectra of decomposition products of formic acid at 374°C, with significant Raman spikes identified by correlated chemical species.


Introduction: Supercritical Reactors + Raman Spectroscopy

• A bottleneck in the process of obtaining conclusive results on the products exiting the system is in the tedious background subtraction processing of the raw data output by the Raman spectrometer.

• Undesirable elements such as background noise from the sample holder, instrument and sample themselves. The baseline may lead to serious problems if the data recorder reaches the detection limits during the practical operation [1].

• Moreover, baseline correction is important since this step extracts the true Raman peak intensities, which are necessary for further numerical processing.

Introduction
Motivation
Methods
Results
  - Automatic Background Subtraction
  - Concentration Analysis
Conclusions and Future Work
Motivation: Time Savings and Increased Accuracy

- Previous to this project all fluorescent background signal was subtracted manually using Origin 2018 software.
- Process was recorded to take 15 - 20 minutes to analyze a single sample’s data
- A study consisting of 16 volunteers Jirasek et al. found that manual baseline determination can not only be influenced by the user’s experience with Raman spectroscopy data, but also the accuracy of baseline determination was negatively effected with a highly sloping baselines [1]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavenumbers of Significant Raman Peaks (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sapphire (Al₂O₃)</td>
<td>379, 418, 751</td>
</tr>
<tr>
<td>Water (H₂O)</td>
<td>1640, 3185</td>
</tr>
<tr>
<td>Formic Acid (HCOOH)</td>
<td>712, 1219, 1400, 1714, 2943</td>
</tr>
<tr>
<td>Hydrogen (H₂)</td>
<td>355, 587, 814, 1034</td>
</tr>
<tr>
<td>Carbon Dioxide (CO₂)</td>
<td>1272, 1383</td>
</tr>
<tr>
<td>Carbon Monoxide (CO)</td>
<td>2138</td>
</tr>
</tbody>
</table>

Introduction
Motivation
Methods
Results
  - Automatic Background Subtraction
  - Concentration Analysis
Conclusions and Future Work
Experimental Methods

- Using the function, ‘textscan’ the integration time, number of averages, laser power, wavelength and raw counts data was extracted and defined suitable variable names.
- The signal was scaled to equivalent laser power and integration time, choosing the strongest signal as the reference.
- The signal was determined by the product of the laser power and integration time.

Schematic of the UW reactor system. The system can operate at pressures up to 35 MPa and temperatures up to 650°C, with residence times of 0.7 – 70 s. The maximum throughput of the system is 41 g of H₂O per minute.
Using Piecewise Cubic Hermite Interpolating Polynomial for Background Subtraction

1. The baseline was created by using predefined anchor points that indicated where the beginning of known substances for Formic Acid

```matlab
%Baseline subtraction
baseline = cell(length(allFiles),1);
subtracted = baseline;
anchor_y = baseline;

%Scale signals to equivalent laser power and integration time, choosing %strongest signal as reference. Strength is determined by the product of %laser power and integration time
strength = zeros(length(allFiles),1);
for i = 1:length(allFiles)
    strength(i) = params{i}(1)*params{i}(3);
end

%Correct for laser power and integration time (strength)
[tmp, index] = max(strength);
for i = 1:length(allFiles)
    y(i) = y(i)*strength(index)./strength(i);
end

%Subtract Baseline
for i = 1:length(allFiles)
    anchor_y[i] = interp1(x[i],y[i],anchor_x);
    baseline[i] = pchip(anchorn_x,anchor_y[i],x[i]);
    subtracted[i] = y[i]-baseline[i];
end
processed = [x subtracted params];
```

2. A for loop was used to scan through the data and using the built in function ‘interp1’ and ‘pchip’ which is used for Piecewise Cubic Hermite Interpolating Polynomial.

3. Once the baseline is created it is subtracted from the raw Raman data to filter out the background spectra and a new variable is defined for the processed data and the output is plotted on a graph along with the baseline and original raw data.

Formic Acid Concentration Analysis

• To find the concentration of formic acid in the products after going through the ScWG reactor a second code was written that interacted with the automatic baseline Matlab script.

• The concentration data is determined using a line of best fit for concentration versus signal intensity.

• The signal used is the ratio of characteristic peak or set of peaks in the reagent to the magnitude of the low-wavenumber sapphire spike that occurs at 418 cm\(^{-1}\).
Introduction
Motivation
Methods
Results
  - Automatic Background Subtraction
  - Concentration Analysis
Conclusions and Future Work
Baseline Subtraction

ME 535 - Final Project - Formic Acid at 400 deg. C and 5 s residence time

- Original Raman Spectra Data
- Least Squares Fit
- Normalized Raman signal

Raman shift, cm⁻¹

Intensity, arb. units
Formic Acid Concentration Analysis

• At a resonance time of zero seconds there is no decomposition of the formic acid so there will be 100% seen by the Ramen cell.

• At 12.5 seconds it was noticed that there was no formic acid left in the system, it had all fully decomposed.

• The amount of five percent formic acid left in the system that didn’t decompose compared to resonance time at 400 degrees Celsius can be seen below in Table 2.

<table>
<thead>
<tr>
<th>Resonance Time (seconds)</th>
<th>Formic Acid in System</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100 %</td>
</tr>
<tr>
<td>2.5</td>
<td>88%</td>
</tr>
<tr>
<td>5</td>
<td>42%</td>
</tr>
<tr>
<td>10</td>
<td>6%</td>
</tr>
<tr>
<td>12.5</td>
<td>0%</td>
</tr>
</tbody>
</table>
Formic Acid Concentration Analysis
Formic Acid Concentration Analysis

- Formic Acid, 2.5 s Residence Time
- Formic Acid, 5 s Residence Time
- Formic Acid, 10 s Residence Time
- Pure Water, No Formic Acid
Introduction
Motivation
Methods
Results
  - Automatic Background Subtraction
  - Concentration Analysis
Future Work and Conclusions
Future Work

• Future experiments will monitor decomposition at a range of residence times for each reaction temperature, to allow for the calculation of kinetic rates and Arrhenius parameters of the decomposition reactions.

• From this study, the Raman spectra of formic acid, H2, CO2, CO, sapphire, and water are known, but future studies involving more complex decomposition pathways will require the methodical identification of Raman spectra of intermediate species.

• This will be accomplished by sequentially gasifying increasingly complex molecules.
Conclusions

1. In this study, formic acid gasification in a continuous supercritical water reactor was studied at temperatures of 400°C using a new background subtraction and concentration Matlab Code.

2. Reaction products were identified as H2, CO2, CO, and residual formic acid from known Raman peaks observed in collected spectra at different resonance times.

3. Supercritical water gasification is a promising technology for the destruction of waste products and the production of useful compounds and fuels.

4. Extensive detail as well as a literature study can be seen in final report document.
Acknowledgements

• The course instructor - Prof. Ashley Emery
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