Thermo-Gravimetric Analysis (TGA) of Combustion and Gasification of Styrene-Butadiene Copolymer (SBR)

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Presentation

- Introduction
- Experimental Setup
- Results
  - Experimental
  - Modeling
- Conclusions
- Future Work
Introduction

- Approximately 270 million tires disposed in U.S.
- Tires do not biodegrade
- Reprocessing is very energy intensive because of strength and makeup
- Makeup (rubber and inorganic content) are well suited for energy production and material recovery
Objectives

- Understand the thermal decomposition process of tires under various conditions
  - Various atmospheres
  - Particle size (mass burn vs other)
  - Primary reaction mechanisms

- Determine/develop higher efficiency, lower emission firing techniques
  - Exhaust gas recirculation
  - Placement of fuel and air injection
  - Enhancement techniques

- Conduct realistic simulations for technology evaluation and application development
Experimental Setup

- **Tire Composition**
  - Natural Rubber
  - Poly-isoprenes
  - Carbon Black
  - Sulfur
  - Inerts and metals

- **Major synthetic rubbers**
  - *Styrene Butadiene Rubber (SBR)*
  - Styrene rubber (SR)
  - Butadiene Rubber (BR)
Experimental Setup

Heated tubing (120°C)

Const. Temperature
Water circulation

Micro-GC

Calibrated Rotometers

Certified gases (pure and mixtures)

N₂
O₂
H₂

80ml/min
20ml/min

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Experimental Conditions

Current conditions found in combustors
- Gasification/ pyrolysis (100% N₂)
- Air atmosphere (20% O₂, 80% N₂)
- Lean atmosphere (6% O₂, 94% N₂)

Possible enhancements for higher efficiency
- Enriched atmosphere (30% O₂, 70% N₂)
- Hydrogen “spiking” (3% H₂, 97% N₂)
Thermal degradation for SBR in N_2

\[ \int (DTA) \, dt = \alpha \] Weight loss fraction

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Combustion Comparisons

Temperature (°C)

350 400 450 500 550 600

Mass (%)

0 10 20 30 40

6.9% O₂

Air

30% O₂

6.9% O₂

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Chemical Structure of SBR;
25% Styrene, 75% Butadiene Cross linked Co-Polymer
Gas Analysis from TGA; N\textsubscript{2} Atmosphere, 20K/min

- **n-Butane**
- **Ethylene**
- **Hydrogen**
- **n-Hexane**
Hydrogen Spiking

10 K/min
Little enhancement

40 K/min
Increased enhancement

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Kinetic Expression Development

\[ \alpha = \frac{W(t) - W_i}{W_i - W_f} \]

\[ \frac{d\alpha}{dt} = k(1 - \alpha)^n \]

\[ k = A T^n \exp\left(\frac{-E}{RT}\right) \]

\[ \frac{d\alpha}{dT} = \frac{A_0}{\beta} T^{1/2} (1 - \alpha)^n \exp\left(\frac{-E}{RT}\right) \]

\[ \frac{d^2\alpha}{dT^2} = \frac{1}{\beta} \left( \frac{d\alpha}{dt} \right) \left[ n(1 - \alpha)^{-1} \left( -\frac{d\alpha}{dT} \right) - \frac{E}{RT^2} + \frac{1}{2} T^{-1} \right] \]

Reaction Order Calc.

Activation Energy Calc.

\[ n = \frac{\beta \left( \frac{d^2\alpha}{dT^2} \right) / \left( \frac{d\alpha}{dt} \right) - E / RT^2 - 1/2 T^{-1}}{\left( -\frac{d\alpha}{dT} \right)} \left( 1 - \alpha \right) \]

\[ E = RT \ln \left[ \frac{\left( \frac{d\alpha}{dt} \right)}{A_0 T^{1/2} (1 - \alpha)^n} \right] \]
## Kinetic Expression Development

**Factors, \( A_0 \) [s\(^{-1} \) k\(^{-1/2}\)]**

| Heating rate, \( \beta \) [K/min] | 100\% N\(_2\) | 97\% N\(_2\) + 3\% H\(_2\) | Air | \( \text{O}_2 \) enhanced |
|-----------------------------------|----------------|----------------|------|----------------|----------------|
| 10                                | 4.02E+12       | 2.55E+11       | 4.64E+09 | 2.87E+11       |
| 20                                | 3.84E+12       | 2.42E+11       | 4.39E+09 | 2.72E+11       |
| 30                                | 3.71E+12       | 2.36E+11       | 4.24E+09 | 2.66E+11       |
| 40                                | 3.67E+12       | 2.30E+11       | 4.13E+09 | 2.59E+11       |

**Graphical Representation**

- **Heating rate, \( \beta \) [K/min]**
- **\( \ln \beta \)**
- **Factors, \( A_0 \) [s\(^{-1} \) k\(^{-1/2}\)]**

**Legend**
- **Primary 100\% N\(_2\)**
- **Primary 97\% N\(_2\) + 3\% H\(_2\)**
- **Primary air**
- **Secondary air**
- **Primary 70\% N\(_2\) / 30\% O\(_2\)**
- **Secondary 70\% N\(_2\) / 30\% O\(_2\)**

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## Summary of Kinetic Parameters

### Activation energy [J/mol]

<table>
<thead>
<tr>
<th>Heating rate, $\beta$ [K/min]</th>
<th>$97% \text{ N}_2 + 3% \text{ H}_2$</th>
<th>Air</th>
<th>$\text{O}_2$ enhanced</th>
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<tr>
<td><strong>AVG</strong></td>
<td><strong>1.87E+05</strong></td>
<td><strong>1.63E+05</strong></td>
<td><strong>1.82E+05</strong></td>
</tr>
</tbody>
</table>

### Overall reaction order, n [-]

<table>
<thead>
<tr>
<th>Heating rate, $\beta$ [K/min]</th>
<th>$97% \text{ N}_2 + 3% \text{ H}_2$</th>
<th>Air</th>
<th>$\text{O}_2$ enhanced</th>
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<td><strong>AVG</strong></td>
<td><strong>1.28</strong></td>
<td><strong>1.19</strong></td>
<td><strong>0.24</strong></td>
</tr>
</tbody>
</table>
Polycyclic Aromatic Hydrocarbon (PAH) (detected to date)

Styrene
Phenanthrene
Naphthalene
Anthracene
Pyrene

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Aspen™ Kinetic Simulation

- **Combustion**\(^2\)
  
  \[
  \text{Tire} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \Delta H_r = -35 \text{ MJ/kg}
  \]

- **Boudouard**\(^3\)
  
  \[
  \text{C}_\text{(s)} + \text{CO}_2 \rightarrow 2 \text{ CO} \quad \Delta H_r = 11 \text{ MJ/kg}
  \]

- **Steam reforming**\(^3\)
  
  \[
  \text{C}_\text{(s)} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \quad \Delta H_r = 14 \text{ MJ/kg}
  \]

- **Water-gas shift**\(^3\)
  
  \[
  \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \Delta H_r = -1.5 \text{ MJ/kg}
  \]
Reisman JI, Lemieux PM. “Air emissions from scrap tire combustion.” Clean Air Technology Center EPA, 1997.
Simulation Results

Combustion

Gasification

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Combustion-Gasification System

1º Air

Sludge/Tire Mixture

Tires

Combustion Zone
(Tire + O₂ → CO₂ + H₂O + heat)

Syngas

Gasification Zone
(C + H₂O + CO₂ + heat → CO + H₂)

2º Air

Ash

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Conclusion

- The two-stage combustion of the SBR is due to the different oxidation rates of the unsaturated hydrocarbon backbone.
- Hydrogen spiking shows enhancements at high heating rates (likely found in combustors)
- Simulations match closely to experiments, refinements needed
- Potential for PAH formation during combustion
Future Work

- Investigation will consist of GC/MS analysis of different atmospheres.
- The study of formation of Polycyclic Aromatic Hydrocarbon (PAH) will be carried out.
- Further development of mechanistic understanding.
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