TGA
Decomposition Kinetics

Decomposition Kinetics Background

- Includes isothermal and constant heating rate methods.

- Constant heating rate method is the fastest and will be discussed here.


- Ultimate benefit obtained in ‘Life-Time’ plots.
Kinetic Analysis

- The rate at which a kinetic process proceeds depends not only on the temperature the specimen is at, but also the time it has spent at that temperature.

- Typically kinetic analysis is concerned with obtaining parameters such as activation energy ($E_a$), reaction order ($k$), etc. and/or with generating predictive curves.
Kinetic Analysis, con’t.

Activation energy ($E_a$) can be defined as the minimum amount of energy needed to initiate a chemical process.

With Modulated TGA, $E_a$ can be measured directly.

TGA Kinetics - Wire Insulation Thermal Stability

Wire Insulation Thermal Stability

Conversion

Temperature (°C)

WEIGHT LOSS (%)

size: 60mg
atm.: $N_2$

100 95 90 85 80

200 250 300 350 400 450 500

6.5% 1.0% 2.8%

6.0% 5% 10% 20%
TGA Kinetics - Heating Rate vs. Temperature

Activation Energy ($E_a$) $\propto$ Slope

TGA Kinetics - Estimated Lifetime

ESTIMATED LIFE (hr.)

ESTIMATED LIFE

TEMPERATURE (°C)

1 century

1 decade

1 yr.

1 mo.

1 week

1 day
Thermogravimetry Under Extreme High Heating Rate Conditions

What Constitutes Extreme Conditions?

- High Heating Rates
- Kinetic Studies
- Sample Throughput
Rapid Heating Thermal Analysis

- Gasification, combustion, and volatilization are complex processes.
- Thermal treatments by different heating rates and time/temperature relationships can result in different chemical decomposition products.
- As an example, heating at a high rate can result in the thermal degradation of component that would otherwise volatilize at a slow heating rate.
- Rapid heating rates, as on the TA Instruments Discovery TGA and pyrolysis GC/MS, provide powerful techniques to investigate the time/temperature relationships.
DTGA Ballistic Heating Performance

Equilibrate method segment is very repeatable and achieves rates approaching 2000°C/min in this application.

DTGA Heating Rate Comparison - Temperature

500°C/min

20°C/min
DTGA Heating Rate Comparison - Time

20°C/min
500°C/min

High Heating Rate TGA: Kinetic Studies
Effect of Heating Rate on Decomposition Temperature of Polystyrene

![Graph showing the effect of heating rate on decomposition temperature of polystyrene.](image)

TGA: Copier Paper in Air

![Graph showing thermal gravimetric analysis of copier paper in air.](image)
### TGA: Quantitation of Copier Paper

<table>
<thead>
<tr>
<th>HEATING RATE °C/min</th>
<th>BREAK RATE weight %</th>
<th>PLATEAU RATE weight %</th>
<th>RESIDUE RATE weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>40.63</td>
<td>16.32</td>
<td>9.87</td>
</tr>
<tr>
<td>1</td>
<td>41.09</td>
<td>16.64</td>
<td>9.85</td>
</tr>
<tr>
<td>2.3</td>
<td>41.27</td>
<td>16.70</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>41.55</td>
<td>16.66</td>
<td>9.79</td>
</tr>
<tr>
<td>10</td>
<td>41.82</td>
<td>16.57</td>
<td>9.74</td>
</tr>
<tr>
<td>23</td>
<td>41.40</td>
<td>16.63</td>
<td>9.90</td>
</tr>
<tr>
<td>50</td>
<td>40.35</td>
<td>16.70</td>
<td>9.88</td>
</tr>
<tr>
<td>100</td>
<td>37.67</td>
<td>17.06</td>
<td>10.08</td>
</tr>
<tr>
<td>230</td>
<td>33.53</td>
<td>16.68</td>
<td>9.83</td>
</tr>
<tr>
<td>500</td>
<td>31.46</td>
<td>-</td>
<td>9.77</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Equilibrate</td>
<td>25.06</td>
<td>-</td>
<td>9.66</td>
</tr>
<tr>
<td>&gt; 2300 °C/min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>41.29</td>
<td>16.66</td>
<td>9.84</td>
</tr>
<tr>
<td>STD DEV</td>
<td>0.41</td>
<td>0.19</td>
<td>0.11</td>
</tr>
</tbody>
</table>

### TGA: Semi-Log Plot of Copier Paper

![Semi-Log Plot of Copier Paper](image-url)

- Equilibrate
- > 2000 °C/min
- 6 Seconds
- 10 Minutes
- 16.7 Hours

* No data at 1000 °C/min
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>400</td>
<td>80</td>
</tr>
<tr>
<td>600</td>
<td>60</td>
</tr>
<tr>
<td>800</td>
<td>40</td>
</tr>
<tr>
<td>1000</td>
<td>20</td>
</tr>
</tbody>
</table>

TGA: High Heating Rates of Copier Paper

Modulated TGA Technology

A New Approach for Obtaining Kinetic Parameters
Temperature Change in MDSC and MTGA

MTGA OF 60% EVA WITH LINEAR RAMP

ACTUAL MEASURED TEMPERATURE

CALCULATED AVERAGE TEMPERATURE

TGA Modulated

Weight (%) vs. Temperature (℃)

Deriv. Modulated Weight (%/min) vs. Temperature (℃)
\[
\frac{d\alpha}{dt} = C \frac{dT}{dt} + f(t,T)
\]

Rate of Weight Loss Zero Kinetic Component

ARRHENIUS AND GENERAL RATE EQUATIONS

\[
\frac{d\alpha}{dt} = k(T) [f(\alpha)] = Z [f(\alpha)] e^{(-E/RT)}
\]

Where:
- \(\alpha\) = reaction fraction
- \(\frac{d\alpha}{dt}\) = rate of reaction
- \(k(T)\) = rate constant at temperature \(T\)
- \(T\) = absolute temperature
- \(f(\alpha)\) = kinetic expression
- \(Z\) = pre-exponential factor
- \(e\) = natural logarithm base
- \(E\) = activation energy
- \(R\) = gas constant
KINETIC EXPRESSION RATIO

\[
\frac{d\alpha_1}{dt} = Z \left[ \tilde{f}(\alpha_1) \right] e^{\frac{E}{RT_1}}
\]

\[
\frac{d\alpha_2}{dt} = Z \left[ \tilde{f}(\alpha_2) \right] e^{\frac{E}{RT_2}}
\]

\[
\frac{d\alpha_1}{d\alpha_2} = \frac{\tilde{f}(\alpha_1)}{\tilde{f}(\alpha_2)} e^{\frac{E}{R(T_2 - T_1)}}
\]

Where:
- \( d\alpha_1 \) = rate of weight loss at temperature \( T_1 \)
- \( d\alpha_2 \) = rate of weight loss at temperature \( T_2 \)
- \( \tilde{f}(\alpha_1) \) = kinetic expression at the value of \( d\alpha_1 \)
- \( \tilde{f}(\alpha_2) \) = kinetic expression at the value of \( d\alpha_2 \)

FACTOR JUMP EQUATION AT CONSTANT CONVERSION

\[
E = \frac{R T_1 T_2 \ln(d\alpha_1 / d\alpha_2)}{T_1 - T_2}
\]

Where:
- \( d\alpha_1 \) = rate of weight loss at temperature \( T_1 \)
- \( d\alpha_2 \) = rate of weight loss at temperature \( T_2 \)
- \( R \) = gas constant
FOURIER TRANSFORMATION YIELDS

\[ T_1 = T + A, \]
\[ T_2 = T - A, \]
\[ L = \ln(\alpha_1 / \alpha_2), \text{ and} \]
\[ f(\alpha_1) = f(\alpha_2) \Rightarrow \ln[f(\alpha_2)/f(\alpha_1)]=0 \]

Where:  
\[ T = \text{average temperature} \]
\[ A = \text{temperature (half) amplitude} \]
\[ L = \text{(full) amplitude of} \]
\[ \ln (\text{rate of weight change}) \]

MODULATED TGA EQUATION

\[ E = \frac{R(T^2 - A^2) L}{2A} \]

Where:  
\[ E = \text{activation energy} \]
\[ R = \text{gas constant} \]
\[ T = \text{average temperature} \]
\[ A = \text{temperature (half) amplitude} \]
\[ L = \ln (\alpha_1 / \alpha_2) = \text{amplitude of} \]
\[ \ln (\text{rate of weight change}) \]
\begin{align*}
\ln Z &= \ln \left[ \frac{d\alpha}{1-\alpha} \right] + \frac{E}{(R \ T)} \\
\text{Where:} & \quad Z = \text{pre-exponential factor} \\
& \quad E = \text{activation energy} \\
& \quad R = \text{gas constant} \\
& \quad T = \text{temperature} \\
& \quad d\alpha = \text{rate of weight loss} \\
& \quad (1-\alpha) = \text{weight fraction}
\end{align*}

- Fast Fourier Transformation yields continuous kinetic parameters
LINEAR HEATING PROFILE FOR POLYTETRAFLUOROETHYLENE

TGA: MTGA - Activation Energy for Polytetrafluoroethylene
EVA(60% Vac)の分解活化能温度歷程圖

EFFECT OF TEMPERATURE ON ACTIVATION ENERGY OF 60% EVA

EFFECT OF CONVERSION ON ACTIVATION ENERGY

TGA Modulated

Poly (60% ethylene vinyl acetate)
Polystyrene
1, 4-Diphenylbutadiyne
MTGA OF 60% EVA WITH DYNAMIC HEATING RATE

MTGA REPEATABILITY POLY (60% ETHYLENE VINYL ACETATE)

<table>
<thead>
<tr>
<th>Side Group Loss</th>
<th>Backbone Decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation Energy (kJ/mol)</td>
<td>Log Pre-Exponential Factor (1/min)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>166.2</td>
<td>13.141</td>
</tr>
<tr>
<td>165.6</td>
<td>13.191</td>
</tr>
<tr>
<td>163.4</td>
<td>13.041</td>
</tr>
<tr>
<td>171.7</td>
<td>13.381</td>
</tr>
<tr>
<td>168.3</td>
<td>13.351</td>
</tr>
<tr>
<td>163.9</td>
<td>12.951</td>
</tr>
</tbody>
</table>

| mean  | 166.5 | 173.9 |
| std. dev. | 3.1 | 2.0 |
| RSD | 1.9% | 1.2% |
MTGA EXPERIMENTAL CONDITIONS

- **Period**: > 200 seconds (temperature range dependent)

- **Amplitude**: 4 - 5 °C

- **Cycles Across Transition**: > 5

**Temperature Program**
- Isothermal or
- Heating Rate: < 2 °C/min

---

**MTGA KINETICS COMPARISON**

<table>
<thead>
<tr>
<th></th>
<th>Activation Energy (kJ/mol)</th>
<th>Logarithm of Pre-Exponential Factor (1/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ASTM E1641</td>
<td>MTGA</td>
</tr>
<tr>
<td>Poly(ethylene)</td>
<td>190</td>
<td>190</td>
</tr>
<tr>
<td>Poly(tetrafluoroethylene)</td>
<td>316</td>
<td>341</td>
</tr>
<tr>
<td>Poly(styrene)</td>
<td>173</td>
<td>182</td>
</tr>
<tr>
<td>Poly(ethylene vinyl acetate)</td>
<td>183</td>
<td>167</td>
</tr>
<tr>
<td>Dicumyl Peroxide</td>
<td>104</td>
<td>101</td>
</tr>
<tr>
<td>1,3 Diphenylbutadiyne</td>
<td>81</td>
<td>99</td>
</tr>
<tr>
<td>Calcium Oxalate · H₂O</td>
<td>117</td>
<td>121</td>
</tr>
<tr>
<td>Calcium Oxalate</td>
<td>207</td>
<td>194</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>210</td>
<td>188</td>
</tr>
</tbody>
</table>

¹Repeatability RSD = 2.8%  ²Repeatability RSD = 1.7%
DETERMINATION OF FULL WIDTH TEMPERATURE AT HALF HEIGHT

BENEFITS OF MTGA METHOD

- SINGLE EXPERIMENT
- INCREASED PRODUCTIVITY
- MODELFREE
- EASY OF USE
- OBTAIN Z WITH ASSUMPTION OF 1st ORDER MODEL
- COMPLETE KINETIC INFORMATION
- E & Z AS A FUNCTION OF CONVERSION
- FOLLOW PROCESS CHANGES
Evolved Gas Analysis

Why Use Evolved Gas Analysis?

• TGA measures weight changes (quantitative)

• Difficult to separate, identify, and quantify individual degradation products (off-gases)

• Direct coupling to identification techniques (Mass Spec, FTIR) reduces this problem
TGA-EGA: Typical Applications

- Polymers (composition, hazard evaluation, identification)
- Natural Products (contamination in soil, raw material selection {coal, clays})
- Catalysts (product/by-product analysis, conversion efficiency)
- Inorganics (reaction elucidation, stoichiometry, pyrotechnics)
- Pharmaceuticals (stability, residual solvent, formulation)

Q50/Q500 EGA Furnace Schematic

- Quartz Liner
- Off-Gases
- Sample Thermocouple
- Sample Pan
- Low internal Volume ~15ml
- Purge Gas In
- Balance Purge
- mace Core
Mass-Spectrometry Benefits

• Additional information for the interpretation of the reactions in the TGA results

• Sensitive method for the analysis of gaseous reaction products

• Exact control of the furnace atmosphere before starting and during the experiment

• Location of air leaks around the furnace

TGA-Mass Spectroscopy

Advantages:

- Higher sensitivity and wider dynamic range than FTIR (1ppm vs. 10ppm).
- Measures non-IR absorbing gases.
- More rapid response.

Disadvantage:

- Cannot distinguish between isomers. (e.g. N₂ and CO)
FTIR (Fourier transformation infrared spectroscopy):

**Advantages:**
- On-line measurement
- Hydrocarbons are easy to identify

**Disadvantages:**
- No detection of inert gases (no dipole moment)
- Detection of inorganic gases limited
TA Instruments Universal Analysis software supports the importation of MS (trend analysis) and FTIR data (Gram-Schmidt and Chemigram reconstructions), allowing TGA and EGA data to be displayed on a common axis of temperature and/or time.
TGA of Calcium Oxalate

Sample: Calcium Oxalate Monohydrate
Size: 17.6070 mg
Method: RT->1000°C @ 20°C/min

TGA-MS Calcium Oxalate

TGA derivative weight loss
H2O m/e=18
CO m/e=28
CO2 m/e=44
**TGA-MS**

Sample: 583-35-E  
Size: 19.6330 mg

---

**Gas switch from N2 to 2% H2 in N2.**

---

**TGA-MS**

During weight loss, a reaction occurs between H2 in purge and sample in which H2O and HO are produced.

---

**N2 Purge then Switch to 2% H2 in N2**

During weight loss, a reaction occurs between H2 in purge and sample in which H2O and HO are produced.
Smoke Generation in Flame Retarded Polymers (PVC)

Benzene is a component of smoke. Much reduced in the flame retardant sample.

Compositional Analysis by TGA-MS

Sample: EVA (25%)
Size: 5.7390 mg
Heating Rate: 20°C/min

17.45% Acetic Acid
(1.001mg)

% VA = 17.45(86.1/60.1)
% VA = 25%

Hydrocarbon CxHy
m/e 56

Acetic Acid
m/e 60
Thank you for your attention!