Valuable products from End of Life Vehicles (ELV) waste by thermal and thermo-catalytic degradation

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Driving forces

Problem: amount of plastics waste is increasing!

Solution:
1. Prevention
2. Re-using
3. Recycling
4. Energy recovery
5. (Landfill)

Directives:

- **94/62/EC EU Directive**: 50-65% of the packaging waste has to be utilized, even with burning, while 25-45% of it has to be processed by chemical- or mechanical proceeding.

- **2000/53/EK Community Directive**: From 1 January 2015 95% of the waste coming from vehicles’ construction material has to be utilized, 85% in mechanical and 10% in chemical recycling.
Pyrolysis/cracking definition

thermal decomposition of organic material at high temperature in the absence of oxygen

involves chemical change of chemical composition and physical phase

Endothermic

Irreversible

CH₃–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₃

decane

Oxygen ✗ ✅ High temperature

CH₃–CH=CH₂

propene

CH₃–CH₂–CH₂–CH₂–CH₂–CH₂–CH₂–CH₃

heptane

+ Pyrolysis 650 °C

- Cracking
Main aims

To investigate the properties and the effect of 5 different catalysts.

Catalyst properties

Product distribution

Product structure

http://www.explainthatstuff.com/zeolites.html


https://en.wikipedia.org/wiki/Linear_alpha_olefin

5th International Conference on Sustainable Solid Waste Management 21-24.06.2017. Athens, Greece
Construction of cracking

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Batch reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>Atmospheric</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Temperature</td>
<td>425, 485 °C</td>
</tr>
<tr>
<td>Cracking time</td>
<td>17 – 40 min</td>
</tr>
<tr>
<td>Feedstock</td>
<td>ELV („end of life vehicles”)</td>
</tr>
<tr>
<td>Catalyst concentration</td>
<td>5 wt%</td>
</tr>
</tbody>
</table>

Diagram:
- Nitrogen
- Gas flow meter
- Polymer waste & catalyst
- Reactor
- Condenser
- Gas flow meter
- Hydrocarbon gases
- Phase separator
- Pyrolysis oil

Gas flow meter

Pyrolysis oil

Phase separator

Condenser

Hydrocarbon gases

Gas flow meter

Polymer waste & catalyst

Reactor

Nitrogen
Catalysts

ZnSO\(_4\)/MgSO\(_4\)/FeSO\(_4\)/SnCl\(_2\)/Ce(SO\(_4\))\(_2\)  

1 mol/dm\(^3\)  
80 °C, 2 h

Distilled Water

110 °C, 10 h  
600 °C, 3 h

Centrifugation & washing

Drying

Calcination

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(S_{\text{BET}}) (m(^2)/g)</th>
<th>(S_{\text{BJH}}) (m(^2)/g)</th>
<th>(D_{\text{av}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>355.4</td>
<td>90.1</td>
<td>1.74</td>
</tr>
<tr>
<td>Zn/ZSM-5</td>
<td>350.8</td>
<td>110.6</td>
<td>1.80</td>
</tr>
<tr>
<td>Mg/ZSM-5</td>
<td>345.3</td>
<td>109.2</td>
<td>1.80</td>
</tr>
<tr>
<td>Fe(II)/ZSM-5</td>
<td>354.5</td>
<td>111.7</td>
<td>1.81</td>
</tr>
<tr>
<td>Sn/ZSM-5</td>
<td>318.9</td>
<td>105.0</td>
<td>1.92</td>
</tr>
<tr>
<td>Ce/ZSM-5</td>
<td>285.4</td>
<td>91.9</td>
<td>1.79</td>
</tr>
</tbody>
</table>
Pyrolysis yields

• mainly pyrolysis oils and gases

• Sn/ZSM-5: maximum yield of pyrolysis oil and the minimum yield of gases

• Ce/ZSM-5: lowest yield of pyrolysis oil and the highest yield of gases

• volatile products were almost the same, only the ratios of gases and liquids changed
Gases composition

425 °C

485 °C

Yield, %

n-parafin
α-olefin
isomer

Zn/ZSM-5
Mg/ZSM-5
Fe(II)/ZSM-5
Sn/ZSM-5
Ce/ZSM-5

0% 25% 50% 75% 100%

Zn/ZSM-5
Mg/ZSM-5
Fe(II)/ZSM-5
Sn/ZSM-5
Ce/ZSM-5

C1
C2
C3
C4
C5
C6

Yields

C1
C2
C3
C4
C5
C6

425 °C

485 °C

Yield, %

n-parafin
α-olefin
isomer

Zn/ZSM-5
Mg/ZSM-5
Fe(II)/ZSM-5
Sn/ZSM-5
Ce/ZSM-5

0% 25% 50% 75% 100%

Zn/ZSM-5
Mg/ZSM-5
Fe(II)/ZSM-5
Sn/ZSM-5
Ce/ZSM-5

C1
C2
C3
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C5
C6

Yields

C1
C2
C3
C4
C5
C6

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Pyrolysis oil composition

![Graphs showing pyrolysis oil composition at 425 °C and 485 °C.](image_url)

- **425 °C**
  - Zn/ZSM-5
  - Mg/ZSM-5
  - Fe(II)/ZSM-5
  - Sn/ZSM-5
  - Ce/ZSM-5

- **485 °C**
  - Zn/ZSM-5
  - Mg/ZSM-5
  - Fe(II)/ZSM-5
  - Sn/ZSM-5
  - Ce/ZSM-5

**Yield, %**

**C6-10**

**C11-15**

**C16-20**

**C21-25**

**C26-30**

**n-paraffin**

**α-olefin**

**isomer**

**aromatic**
Products

Gas: 43 – 61 %  
Oil: 39 – 57 %  
Residue: ~1 %

- Energy recovery
- Fuel
- Chemical raw materials, eg. styrene or other plastic monomer

- Energy recovery
- Activated carbon raw material
• ELV recycling by pyrolysis
• Main driving forces: waste management & EU directives
• Main aim: to investigate the effect of 5 zeolite based catalysts
• Products further utilization:
  o Most gas: Ce/ZSM-5 (energy recovery)
  o Most pyrolysis oil: Sn/ZSM-5 (fuel)
    ➢ Most aromatics compound: Fe(II)/ZSM-5 (chemical raw material)
    ➢ Most paraffin: Mg/ZSM-5 (wax)
    ➢ Most olefin: Fe(II)/ZSM-5 (chemical synthesis)
Acknowledgements

The authors express their gratitude to the National Office for Research and Innovation, within the framework of support for Hungarian-indian (KTIA-DST) R & D & I co-operation program (TÉT_13_DST) (TÉT_13_DST-1-2014-0003)

Thank you for your attention!