Catalytic pyrolysis of plastic waste: Opportunities and Challenges

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16/05/2022   VTT – beyond the obvious
Content

- The problem of plastic waste
- Plastic recycling methods
- Catalytic pyrolysis
- Case examples
- Conclusions
Why is plastic relevant?

Employment: Close to 1.5 million
Companies: Close to 52 thousand
Turnover: Close to 33 Billion Eur

2020 Plastics Europe estimations – Eurostat official data only available until 2018.
WORLD AND EUROPEAN plastics production evolution

**WORLD PLASTICS PRODUCTION**
These figures do not include the production of recycled plastics

**EUROPEAN PLASTICS PRODUCTION**
These figures do not include the production of recycled plastics
Plastic Circular Economy - Vision
Global flows of plastic packaging materials in 2013

[Diagram showing the flow of plastic packaging materials, including:

- 78 million tonnes (annual production)
- 98% virgin feedstock
- 2% closed-loop recycling
- 8% cascaded recycling
- 4% process losses
- 14% collected for recycling
- 14% incineration and/or energy recovery
- 40% landfilled
- 32% leakage]

Source: Project Mainstream analysis - for details please refer to Appendix A.

VTT plastic recycling platforms

Collection and possible pretreatment

Mechanical recycling
- Valorization, compounding
- Granulation

RECYCLED PLASTIC
- Compounding, granulation

Chemical recycling
- Leaching
  - De-polymerization
- Other chemical recycling
  - Gasification
- Thermochemical recycling
  - Liquefaction
  - Syngas
  - Pyrolysis oil

Polymers
Monomers
- Monomers, chemicals, fuels

Biological & bio-tech recycling
- Composting, (anaerobic) fermentation
- High-tech bio-technology
  - CO₂, H₂O, CH₄; variety of small molecules

Municipal waste
- Industrial waste
- Litter from nature
Thermochemical conversion

Pyrolysis

- Thermal degradation of plastics into liquid fuel components
- Suitable to end of life mechanically non-recyclable plastics
- Valuable hydrocarbons recovered including monomers for re-polymerization
- Heterogeneous plastics treated
- Selectivity and yield can be optimized with the use of a suitable catalyst
- Mild pretreatment needed
- Energy intensive process – process gas recycled
- Moderately large CAPEX
- Post treatment might be needed depending on the contaminants

Pilot examples

- Agilyx (USA)
- Plastic energy (ES)
- Recycling technologies (UK)
- ResPolyflow (USA)
- PHJK (FI)
- Nexus (USA)
What makes catalytic pyrolysis interesting?

**Benefits**
- Lower operating temperature hence lower energy demand
- High product selectivity
- Tuneable products

**Drawbacks**
- Coking/poisoning
- Expensive
- Regeneration/replacement required

TGA profiles

https://doi.org/10.1016/j.enconman.2017.03.071
Thermal vs. catalytic pyrolysis

GC analysis of the product obtained in the LDPE (a) thermal degradation (b) catalytic degradation over HZSM-5 zeolite
Advantages vs. disadvantages of catalytic cracking

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lowering of the reaction temperature, decrease in energy consumption</td>
<td>Catalysts need regeneration/replacement.</td>
</tr>
<tr>
<td>Reaction proceeds faster, bringing about shorter residence times and lower reactor volumes.</td>
<td>Acid solid catalysts can be deactivated by coke deposition and by the occurrence of different cross-linking reactions favoured by the presence of some plastics</td>
</tr>
<tr>
<td>Selectivity may be tailored towards different valuable products by a judicious choice of both the catalyst and process conditions in the case of polyolefins, the products derived from the catalytic cracking contain mainly cyclic, branched and aromatic hydrocarbons, which increase the quality of the potential fuels;</td>
<td>The situation is completely different when real polymer wastes are to be degraded. Heteroatoms such as nitrogen, coming from acrylonitrile–butadiene-styrene plastics (ABS) (among other sources), and sulphur, from oils, rubber and some additives, are usually present in plastic wastes, these compounds are known poisons for acid solids catalysts and decrease their activity to a large extent</td>
</tr>
<tr>
<td>Inhibition of the formation of undesired products (e.g. chlorinated hydrocarbons), which is a feature especially interesting in the presence of PVC</td>
<td>PVC may cause corrosion problems as well as the formation of toxic chlorine containing compounds</td>
</tr>
</tbody>
</table>
Case examples at VTT
Fast pyrolysis of plastics in bench scale bubbling fluidized bed unit

- Capacity of 1 kg/h
- Temperature up to 650 °C
- Nitrogen or a mixture of steam and nitrogen used to fluidized bed material
- Stage-wise condensation:
  - Water cooler: 20 °C
  - Electrostatic precipitator: 20 °C
  - Glycol cooler: - 5 °C
  - Dry ice cooler: - 50 °C
Batch reactor (Lab-scale)

- Batch reactor is heated by an electrical oven that is attached on a mobile rig.
- Batch feeding system uses drop in mechanism of raw materials inside the reactor.
- The rig can be extended to attach another oven and use both batch reactor and a cracking reactor in sequence.
Tuning the product slate


- Thermal 550C 62s
- Y-zeolite 550C 63s
- Montmorillonite 525C 67s

- Liquid yield, wt%
- Wax yield, wt%
- Gas yield, wt%
- Char yield, wt%
- Total mass balance
Comparison of catalyst types

Fixed bed batch pyrolysis at 525 C RT 1min C/F 1:1
Effect of zeolite catalyst acidity, comparison at T 550°C

Feedstock (5g) HDPE:LDPE:PP:PS (1.45:1.75:1.1:0.7)

Plastic to Chemicals with catalysts
# Recovery of highly valuable chemicals

<table>
<thead>
<tr>
<th>Component</th>
<th>Area%</th>
<th>HAcZ</th>
<th>LAcZ</th>
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<tbody>
<tr>
<td>Monoaromatics</td>
<td></td>
<td>91.4</td>
<td>81.7</td>
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<tr>
<td>Non-aromatic</td>
<td>4.3</td>
<td>14.2</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>14.7</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>30.1</td>
<td>20.7</td>
<td></td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>6.0</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>m-xylene</td>
<td>20.6</td>
<td>16.7</td>
<td></td>
</tr>
<tr>
<td>o-xylene/styrene</td>
<td>6.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other monoaromatics</td>
<td>13.6</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>Naphtalenes</td>
<td>4.3</td>
<td>17.3</td>
<td></td>
</tr>
<tr>
<td>Diaromatics</td>
<td>0.0</td>
<td>3.7</td>
<td></td>
</tr>
</tbody>
</table>
Highly olefinic gas

- Medium acidity catalyst lowest temperature 450°C
- Medium acidity catalyst shortest residence time
- Lowest acidity catalyst highest temperature 600°C
Boiling point distribution

Simulated distillation of BR experiments

- Thermal, 525
- Thermal, 500
- Thermal, 550
- ZSM-5, 500
- ZSM-5, 525
- ZSM-5, 550
- Montmo, 500
- Montmo, 550
- Montmo, 525
- Alumina, 500
- Alumina, 525
- Alumina, 550
Decontaminating hazardous plastics

Real WEEE plastic feedstock (PP/PE predominantly)

With Dolomite

WEEE = Waste Electrical and Electrical Equipment
Products from catalytic pyrolysis with dolomite

- With dolomite, a large increase in the liquid yield was observed with steam addition.
- Addition of steam promotes cracking reactions.
Conclusions

- Pyrolysis process imparts flexibility both towards feedstock and required products.
- The use of a right catalyst enables tuning the pyrolysis oil towards fuels, chemicals and monomers.
- The mode of catalysis (in-situ vs. ex-situ) has an impact on the product and catalyst recovery.
- From the economical point of view, only cheap and robust catalysts can have the place in waste management sector.
- Catalysts are easily poisoned by impurities in plastic waste, therefore long term trials are necessary to validate the extended efficiency.
- Downstream processing of the pyrolysis oil also requires the use of a suitable catalyst.
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References

- Image used in the content slide from https://www.advancedsciencenews.com/global-alliance-to-end-plastic-waste/
- https://www.globalcitizen.org/en/content/plastic-pollution-facts/
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