Valorization of Plastic Waste with the Aid of Solar Hydrothermal Liquefaction

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Overview

- Introduction
  - Plastic waste Industry
  - Hydrothermal Liquefaction (HTL) concept
  - The role of water
  - Solar Hydrothermal Liquefaction (SHTL) concept

- Aim and methodology

- Preliminary HTL tests
  - Setup and experimental conditions
  - Experimental results
  - Indicative physico-chemical characterization

- Lab-scale HTL-CST coupling

- Conclusions and future work
Plastic Waste Industry

€UROPE (EU28+NO/CH), 2018

61.8 million tonnes
Plastics production

9.1 million tonnes
Plastic post-consumer waste collected to be recycled

PLASTIC POST-CONSUMER WASTE TREATMENT

- Energy recovery 42.6%
- Landfill 24.9%
- Recycling 32.5%

29.1 million tonnes

Source: PlasticsEurope
Hydrothermal Liquefaction (HTL) concept

- Thermochemical conversion of organic waste into added value products
- Suitable technique for organic waste/byproducts with high moisture
- Treatment at 250 - 500°C & 50 - 250 bar
- Use of a reducing gas and (optionally) a catalyst
- Mostly water (moisture) used as solvent in its subcritical/supercritical condition

Reactant: Organic feedstock + moisture

Process: HTL reactor

Products:
- Biofuel or bio-oil
- Aqueous phase rich in phosphates/nitrates
- Solid organic residue
- Gas phase (primarily CO, CO₂, CH₄)
The role of water

- Triple role as solvent, reactant and catalyst
- Non-polar solvent in appropriate pressure and temperature
- Avoidance of feedstock drying (energy demanding step)

Temperature $\uparrow$ leads to

- Density $\downarrow$
- Dielectric constant $\downarrow$
- Ionization constant ($K_w$) change
Solar energy as a power source

Conceptual HTL & CST coupling flowsheet incl. preprocessing steps & outlet streams

HTL tube reactor & parabolic trough system (used as an example)
Aim of this work – methodology

- Development of a feedstock database based on extensive literature review
- Preliminary HTL tests
  - Choice of different parameters (2 feedstocks, 6 temperatures, 2 initial pressures, 2 product solvents)
  - Initial design concepts for lab- and pilot-scale tests
  - Lab-scale reactor under construction
- Full physico-chemical characterization
- HTL – CST coupling
  - Feedstock incl. algae, agriculture residue, plastics, industrial/municipal sludge etc.
  - Characterization of feedstock and final products (bio-oil, aqueous & gas phases)
Preliminary HTL tests – Setup

- Preprocessing of feedstock (shredding and/or mixing)
- 1.8 L HP/HT SS autoclave reactor
- Electronic controller for temperature & stirring speed regulation
- Use of an electric heater for reactor heating
### Preliminary HTL tests – Experimental conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock</td>
<td>Polypropylene flakes (PP), plastic waste mix (PWM)</td>
</tr>
<tr>
<td>Reducing gas</td>
<td>N₂</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>350, 370, 375, 400, 425, 450</td>
</tr>
<tr>
<td>Initial Pressure (bar)</td>
<td>1, 20</td>
</tr>
<tr>
<td>Residence time (min)</td>
<td>30</td>
</tr>
<tr>
<td>Stirring</td>
<td>Continuous</td>
</tr>
<tr>
<td>Water/waste ratio (wt%)</td>
<td>90/10</td>
</tr>
</tbody>
</table>

![PWM Image](image1.png)

![PP Image](image2.png)
Products separation

Gaseous products  Solvent addition  Filtration  Phase separation  Bio-oil

Products solvents:

- Dichloromethane (CH₂Cl₂, **DCM**) → b.p. 39.6 °C (polar)
- Acetone ((CH₃)₂CO, **DMK**) → b.p. 56.1 °C (partially polar)
- Ethyl acetate (CH₃COOCH₂CH₃, **ETAC**) → b.p. 77.1 °C (polar)

- Acetone was eliminated from further studies, unable to separate different phases
Preliminary HTL tests results (I)

- Bio-oil yield calculation equation

\[
\text{Bio-oil yield(\%)} = \frac{W_{\text{bio-oil}}}{W_{\text{feedstock}}} \times 100
\]

- PWM bio-oil yield (%) for all conditions & different solvents
Preliminary HTL tests results (II)

- PP did not convert into bio-oil at temperatures below 425°C
- Bio-oil in PP case was separated from aqueous phase without use of solvent

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Bio-oil yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400°C – 1 bar</td>
<td>0.0</td>
</tr>
<tr>
<td>425°C – 1 bar</td>
<td>53.8</td>
</tr>
<tr>
<td>450°C – 1 bar</td>
<td>45.4</td>
</tr>
</tbody>
</table>

* Did not convert

- Highest bio-oil yields observed in different experimental conditions, difficult determination of a specific experimental pattern → Bio-oil yield significantly different behavior depending on feedstock’s main components
Physico-chemical characterization

Feedstock

- Negligible moisture content
- 300-500°C decomposition of heavy organics
- Low percentage of inorganics

Thermogravimetric analysis (TGA) of feedstock

Inorganics analysis of plastic waste

<table>
<thead>
<tr>
<th>Inorganic element</th>
<th>Value (mg/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorides</td>
<td>390</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.12</td>
</tr>
<tr>
<td>Sulfates</td>
<td>280</td>
</tr>
<tr>
<td>Copper</td>
<td>0.05</td>
</tr>
<tr>
<td>Fluorides</td>
<td>0.4</td>
</tr>
<tr>
<td>DOC</td>
<td>170</td>
</tr>
<tr>
<td>TDS</td>
<td>840</td>
</tr>
</tbody>
</table>

- Inorganics remaining in aqueous phase could be used in other applications (e.g. as a fertilizer)
Physico-chemical characterization

Products

Gaseous (GC)

<table>
<thead>
<tr>
<th>Gaseous product</th>
<th>CO₂</th>
<th>CH₄</th>
<th>CO</th>
<th>C₂H₄</th>
<th>C₃H₆</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume(*) %</td>
<td>6.04</td>
<td>1.6</td>
<td>1.3</td>
<td>0.2</td>
<td>0.19</td>
<td>0.13</td>
<td>0.12</td>
</tr>
</tbody>
</table>

* The rest gaseous product volume corresponds to N₂

Bio-oil (GC-MS): fatty acids, phenols & long chain alkanes

Indicative compounds of bio-oil (GC-MS):

- Benzene, 1,1'-(1,3propanediyl)bis
- Heptadecane
- Octadecane
- Nonadecane
- Eicosane
- Heptadecane, 2,6,10,15-tetramethyl
- Heneicosane
- 1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-
Lab-scale HTL-CST coupling

- Preliminary tests of solar HTL → Utilization of in-house Solar Simulator
- 4 ellipsoid reflectors with 6kW\textsubscript{el} Xenon arc lamps
- 2L reactor arrangement designed and constructed for HTL-CST coupling tests
Proof of concept verification (II)

- The reactor in Solar Simulator reaches desired temperature and pressure in less than 50% of time compared to the one in the electric heater
- Successful conditions’ stabilization using the Solar Simulator
Conclusions & Future work

- Verification of successful waste feedstock conversion into value added products → **Bio-oil yield up to ~ 50%**
- HTL-CST coupling significantly speeds up the process and greatly reduces energy consumption
- Highest bio-oil yields observed in different experimental conditions predominantly depending on feedstocks’ main components

Future work

- Initial pilot-scale experiments utilizing solar energy to take place within coming months
- Experimental conditions expansion: **presence of catalyst**
- Study of additional feedstock materials incl. agricultural residues, manure & sludge
Acknowledgments

This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code: T1EDK-05079)
Thank you for your attention!

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