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Valorization of Plastic Waste with the Aid of Solar Hydrothermal Liquefaction

Nikolaos I. Tsongidis[1, 2], Charikleia A. Poravou[1,2], Vasiliki A. Zacharopoulou[1], Dimitrios A. Dimitrakis[1], Alexandra Zygogianni[1] and Athanasios G. Konstandopoulos[1, 2]

[1]Aerosol & Particle Technology Laboratory, CPERI/CERTH, Thessaloniki, Greece

[2]Department of Chemical Engineering, Aristotle University of Thessaloniki (AUTH), Thessaloniki, Greece

AEROSOL & PARTICLE TECHNOLOGY LABORATORY

CPERI Chemical Process & Energy Resources Institute

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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

EUROPE (EU28+NO/CH), 2018

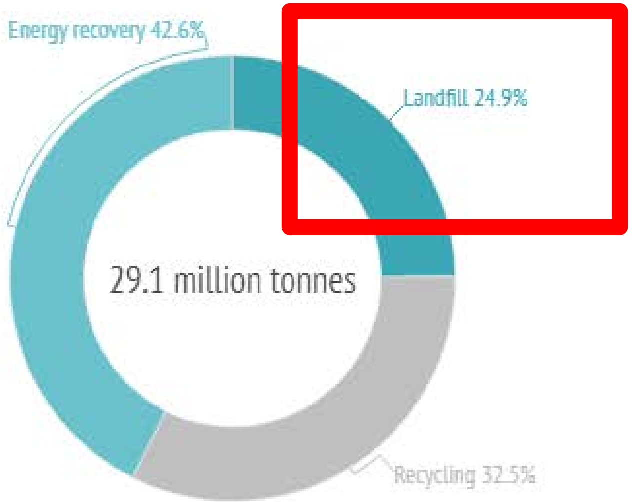
61.8 million tonnes

Plastics production

9.1 million tonnes

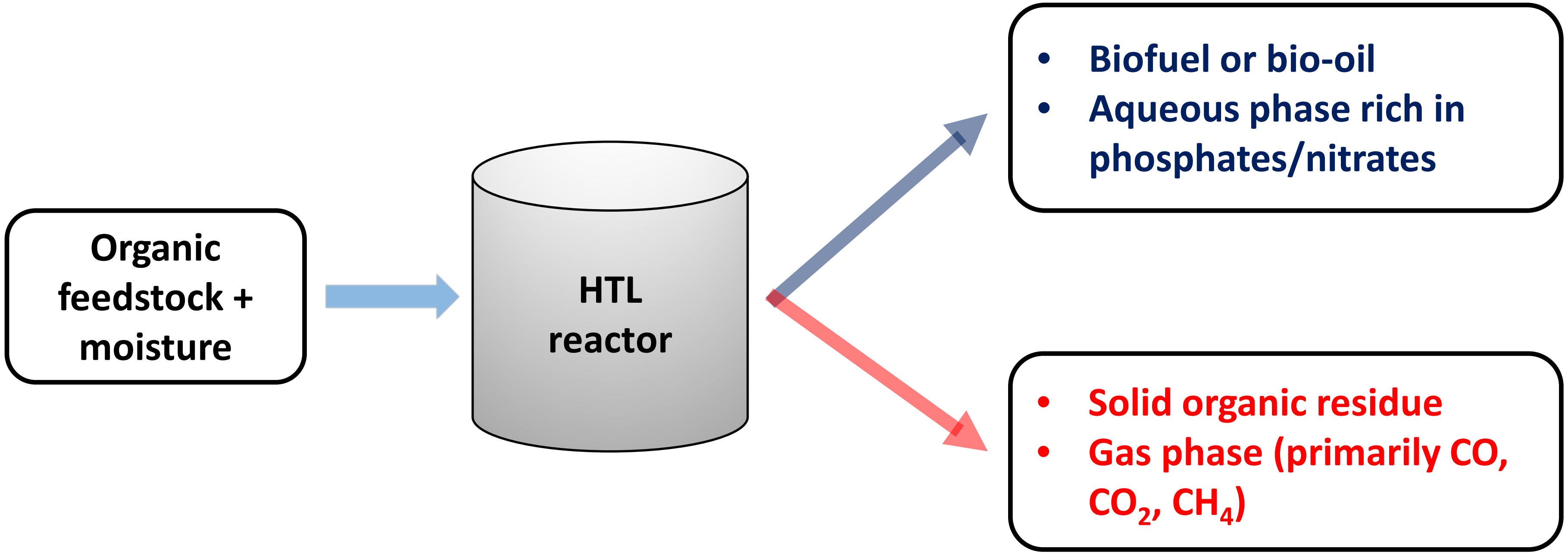
Plastic post-consumer waste collected to be recycled

PLASTIC POST-CONSUMER WASTE TREATMENT



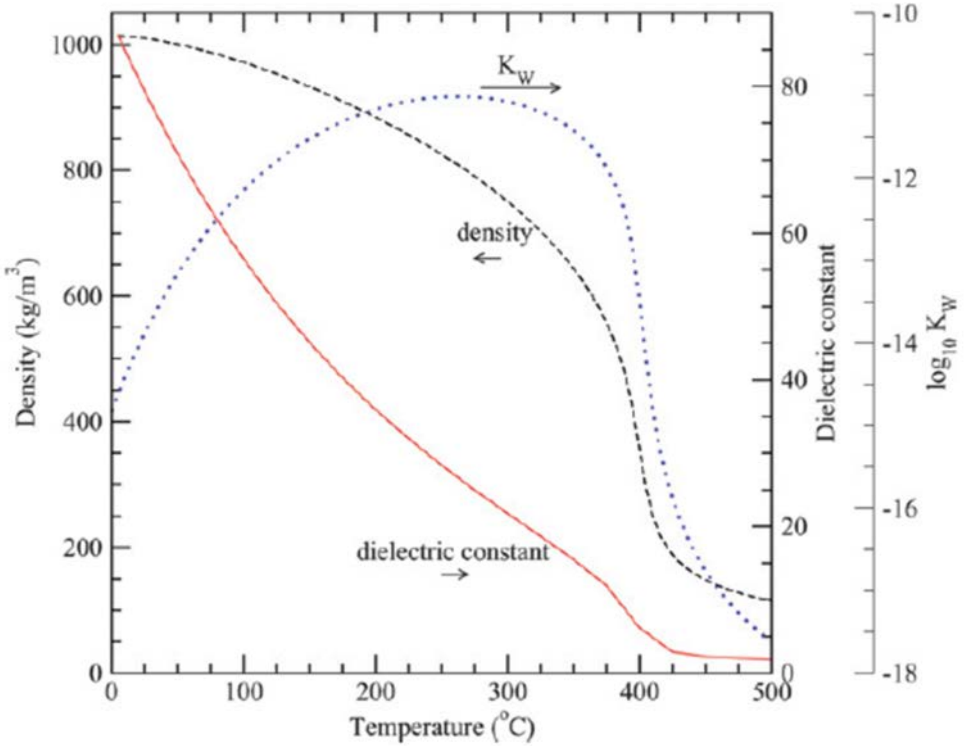
Source: PlasticsEurope

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

The role of water

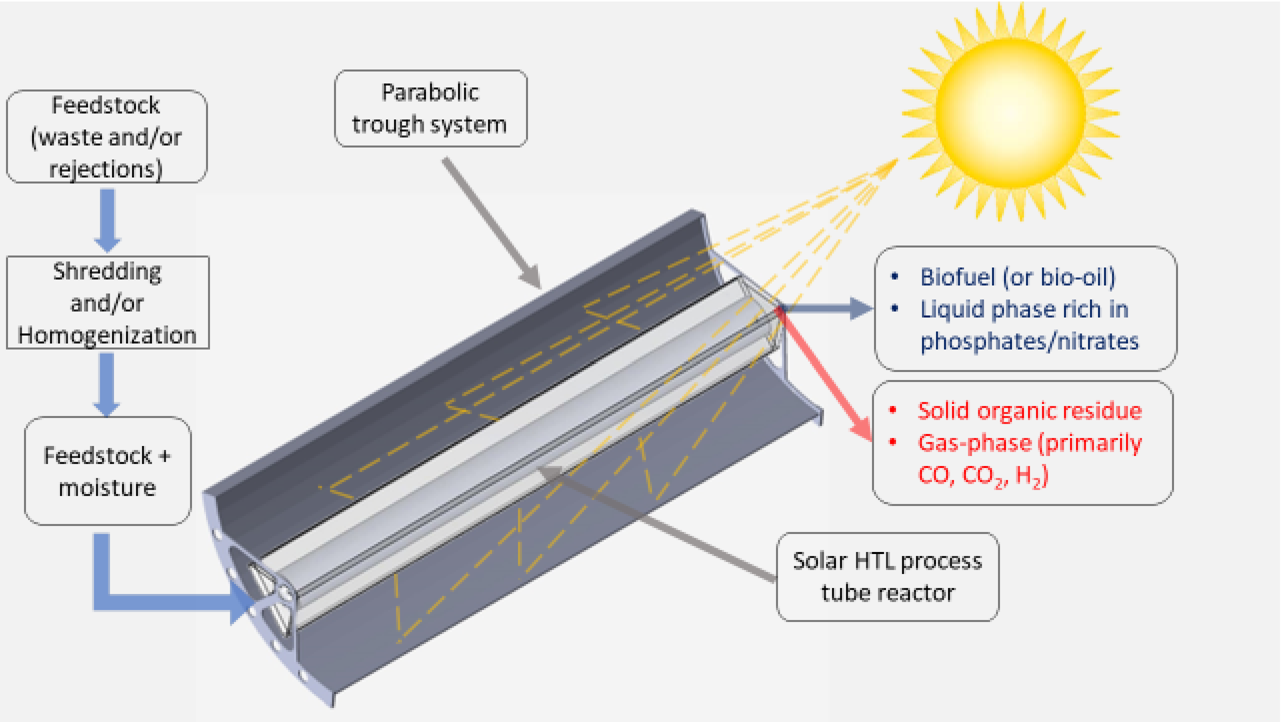


Temperature ↑ leads to

Density ↓
Dielectric constant ↓
Ionization constant (K_w) change

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

Solar Hydrothermal Liquefaction (SHTL) concept

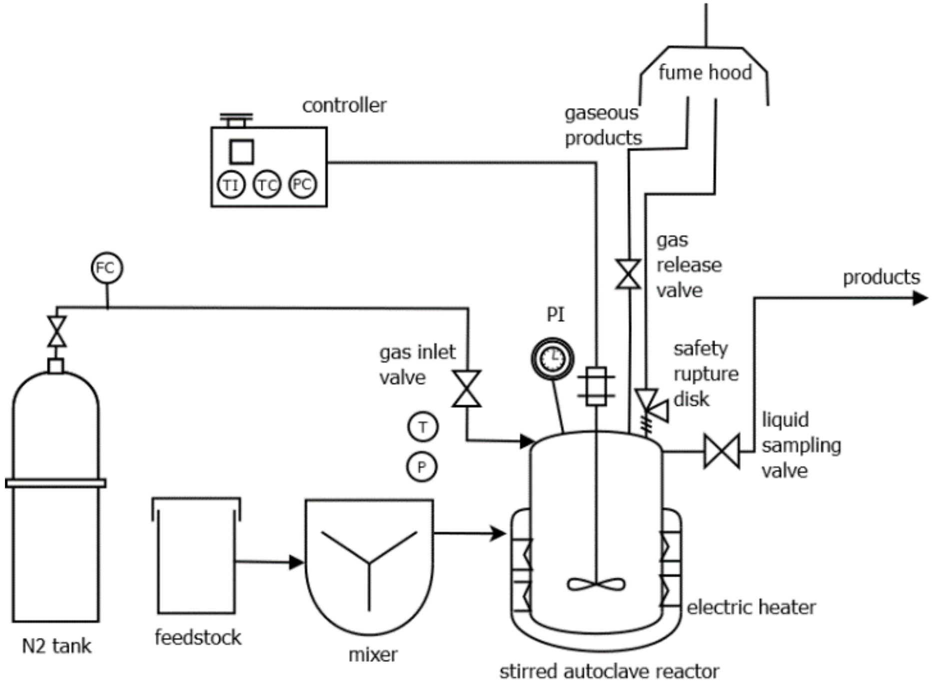


- Solar energy as a power source
- Conceptual HTL & CST coupling flowsheet incl. preprocessing steps & outlet streams
- HTL tube reactor & parabolic trough system (used as an example)

Aim of this work – methodology

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

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

Feedstock	Polypropylene flakes (PP), plastic waste mix (PWM)
Reducing gas	N_2
Temperature (ºC)	350, 370, 375, 400, 425, 450
Initial Pressure (bar)	1, 20
Residence time (min)	30
Stirring	Continuous
Water/waste ratio (wt%)	90/10

PWM

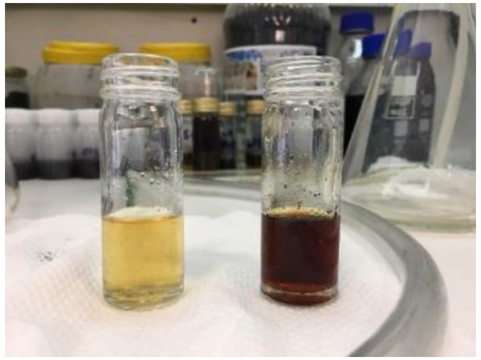
PP

Products separation

Gaseous products

Solvent addition

Filtration



Phase separation

Bio-oil

Products solvents:

- Dichloromethane (CH_2Cl_2, **DCM**) → b.p. 39.6 ^oC (polar)
- Acetone ($(CH_3)_2CO$, **DMK**) → b.p. 56.1 ^oC (partially polar)
- Ethyl acetate ($CH_3COOCH_2CH_3$, **ETAC**) → b.p. 77.1 ^oC (polar)

➢ Acetone was eliminated from further studies, unable to separate different phases

DCM

DMK

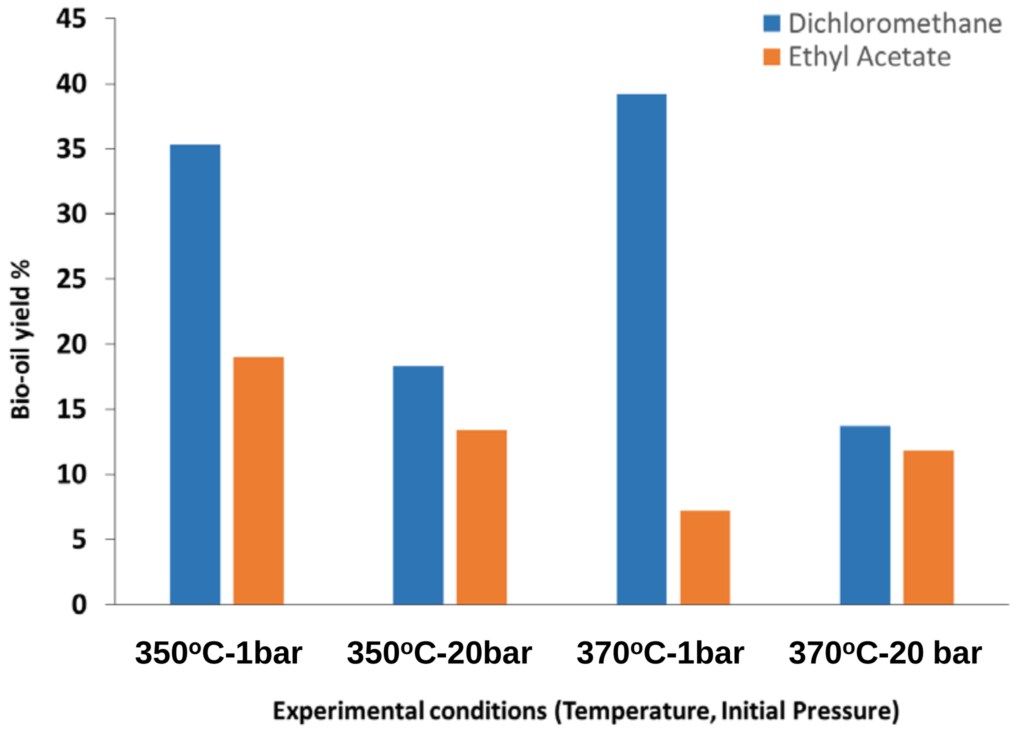
Preliminary HTL tests results (I)

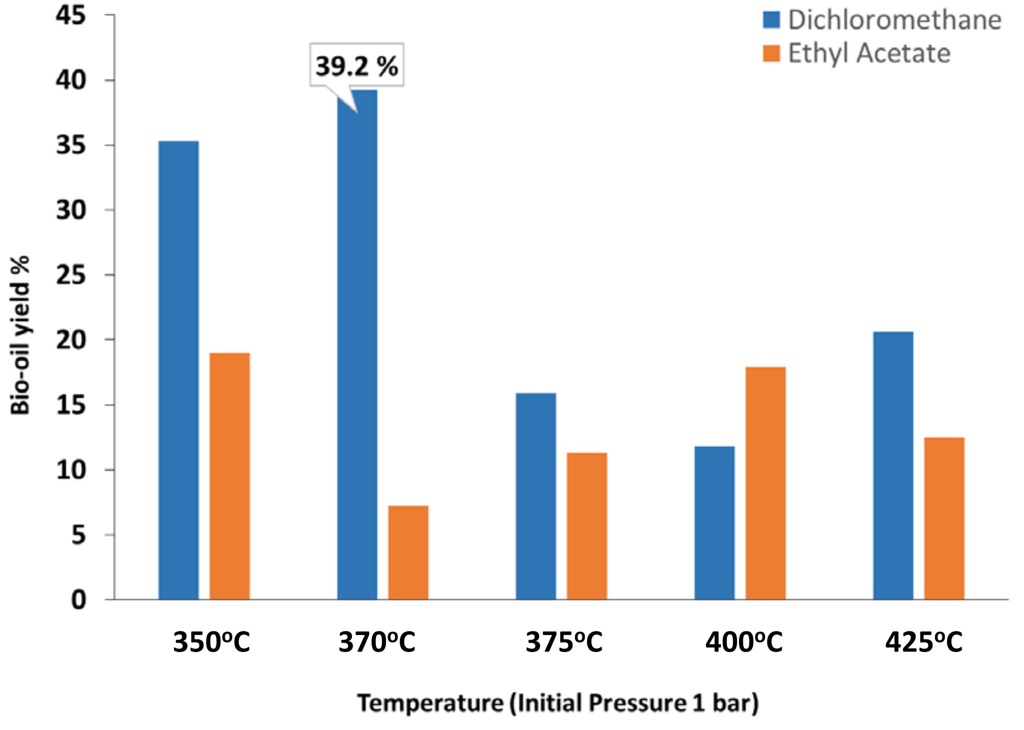
- Bio-oil yield calculation equation

$$\text{Bio} - \text{oil yield}(\%) = \frac{w_{\text{bio-oil}}}{w_{\text{feedstock}}} \text{x } 100$$

$W_{bio\text{-}oil}$: weight of bio-oil (g)
$W_{feedstock}$: weight of dried feedstock (g)

- PWM bio-oil yield (%) for all conditions & different solvents



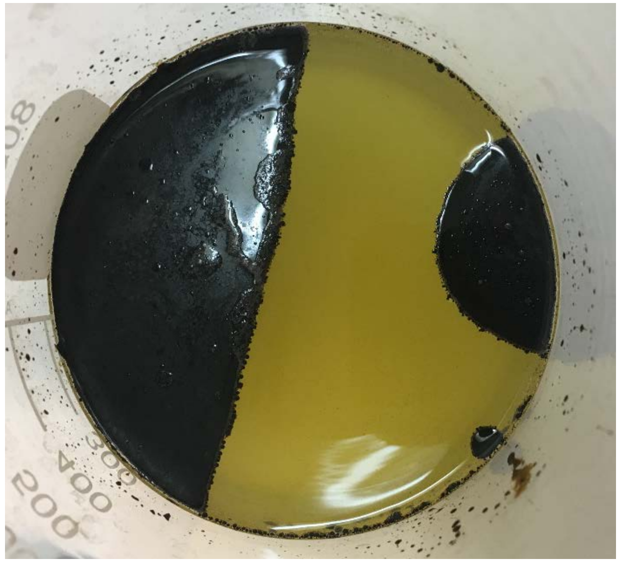


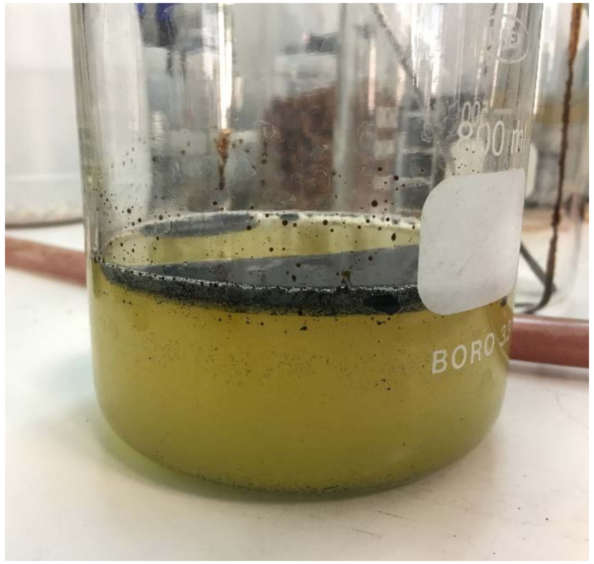
Preliminary HTL tests results (II)

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

Experimental conditions	Bio-oil yield (%)
400ºC – 1 bar	0.0
425ºC – 1 bar	53.8
450ºC – 1 bar	45.4

** Did not convert*



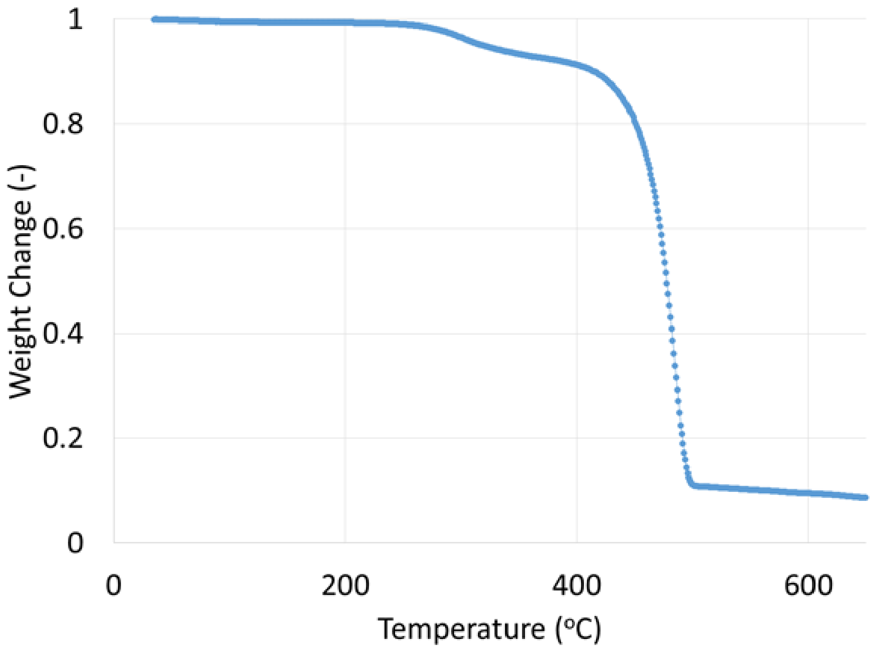


- Highest bio-oil yields observed in different experimental conditions, difficult determination of a specific experimental pattern → Bio-oil yield significantly different behavior depending on feedstock's main components

Physico-chemical characterization

❖ Feedstock

Thermogravimetric analysis (TGA) of feedstock



Inorganics analysis of plastic waste

Inorganic element	**Value (mg/Kg)**
Chlorides	390
Zinc	0.12
Sulfates	280
Copper	0.05
Fluorides	0.4
DOC	170
TDS	840

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

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

Physico-chemical characterization

❖ Products

Gaseous (GC)

Gaseous product	CO_2	CH_4	CO	C_2H_4	C_3H_6	C_2H_6	C_3H_8
Volume[(*)] %	6.04	1.6	1.3	0.2	0.19	0.13	0.12

** The rest gaseous product volume corresponds to N_2*

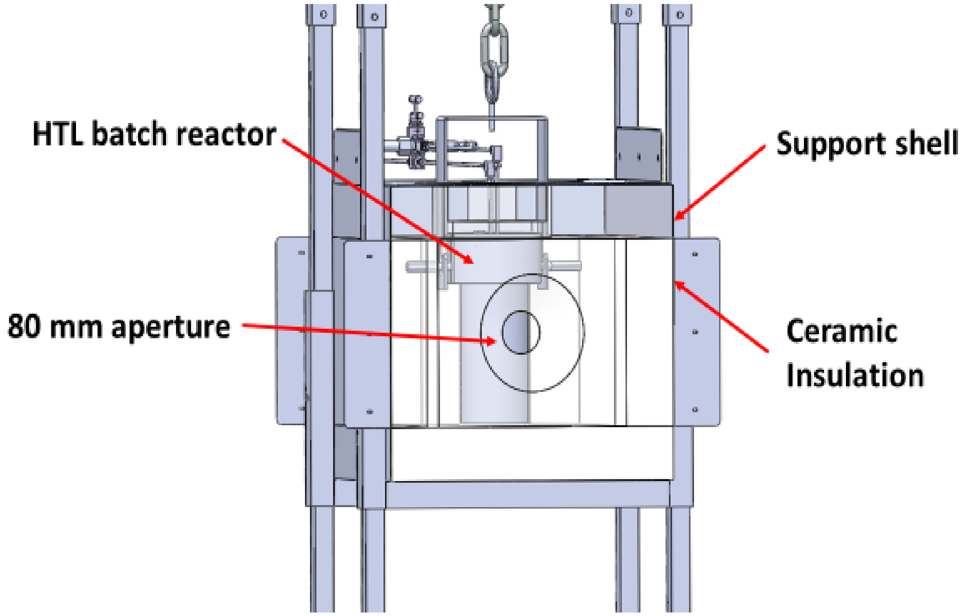
Bio-oil (GC-MS): fatty acids, phenols & long chain alkanes

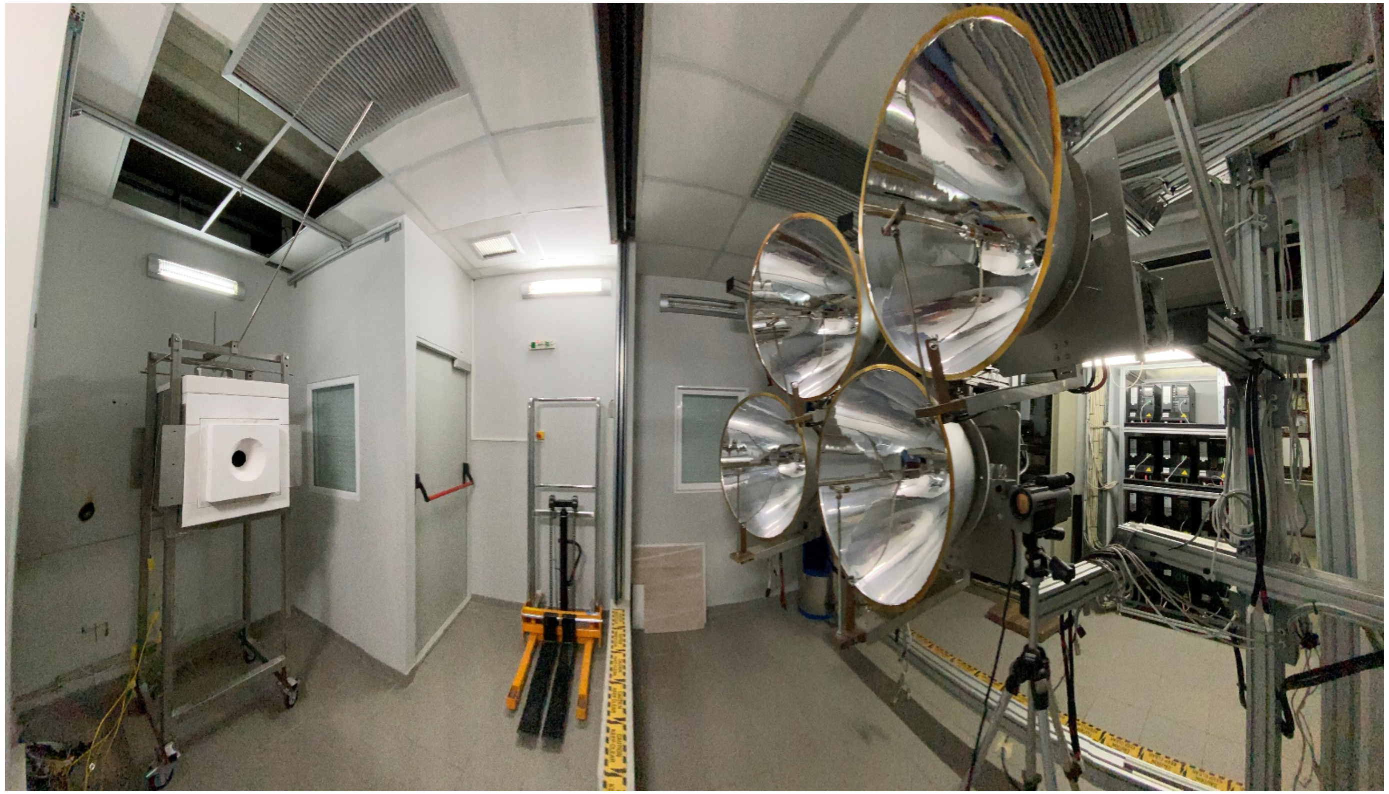
Indicative compounds of bio-oil (GC-MS):

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

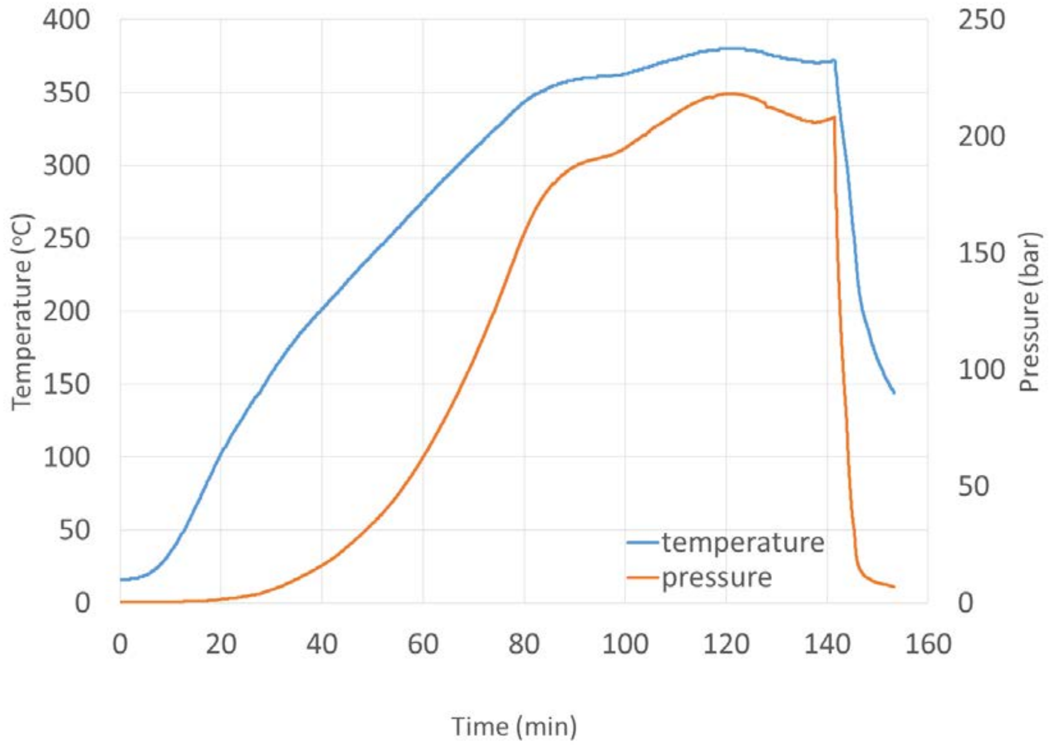
- Preliminary tests of solar HTL → Utilization of in-house Solar Simulator
- 4 ellipsoid reflectors with 6kW$_{el}$ Xenon arc lamps
- 2L reactor arrangement designed and constructed for HTL-CST coupling tests



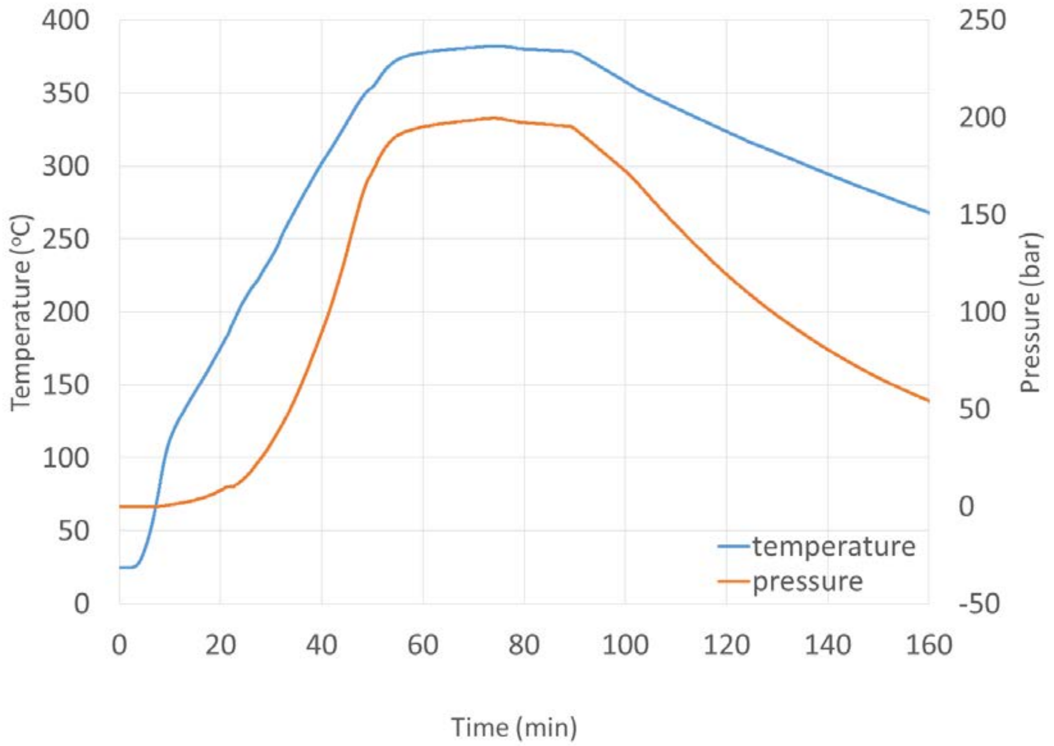


Proof of concept verification (II)

❖ **Electric heater**



❖ **Solar Simulator**



- 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

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Ευρωπαϊκή Ένωση
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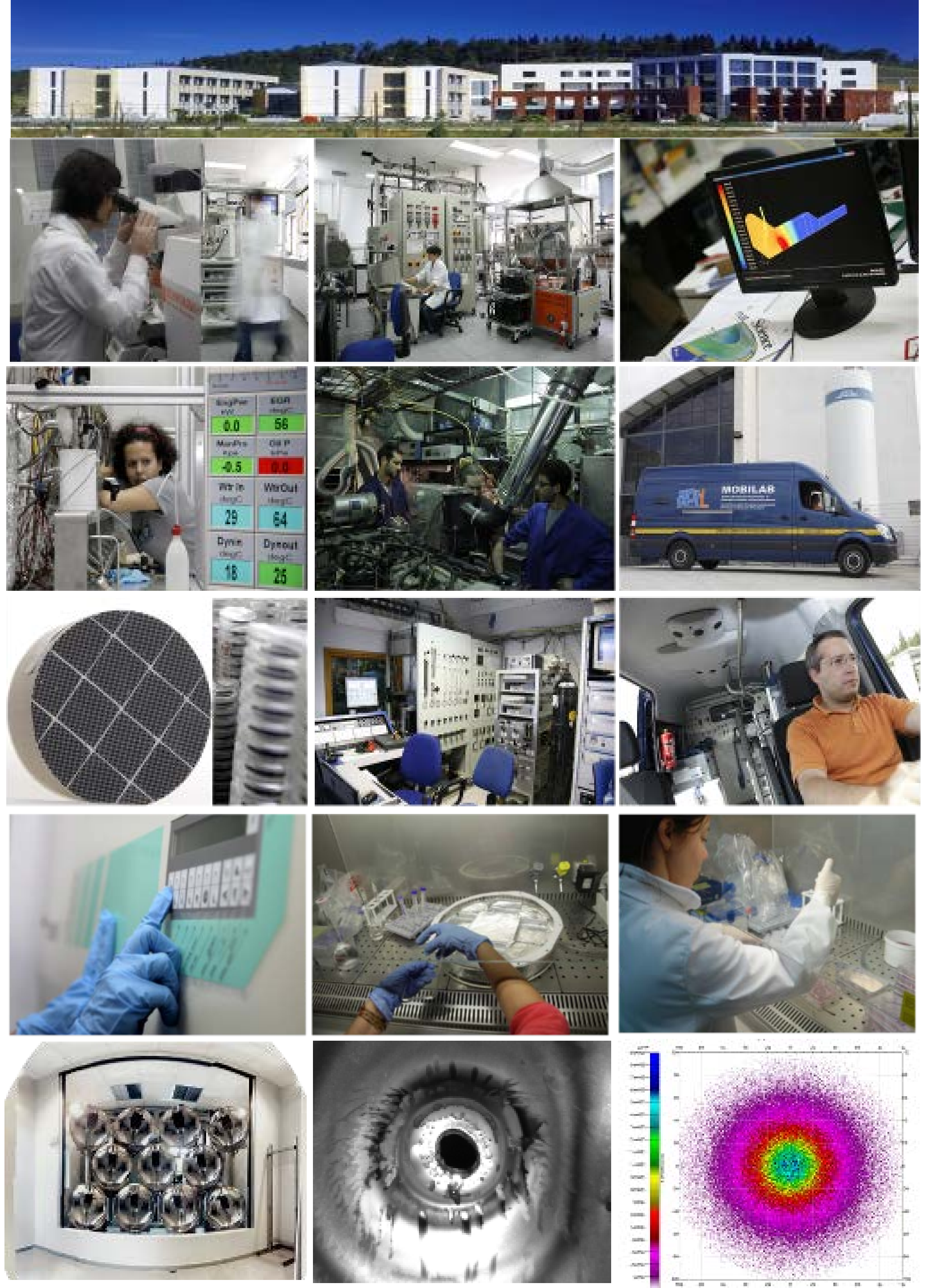
Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης



Thank you for your attention!

AEROSOL & PARTICLE TECHNOLOGY LABORATORY

cporavou@certh.gr;
agk@certh.gr

http://apt.cperi.certh.gr