EUSHIPPINGBCE
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HydroProcessing HydPro group

# Low carbon fuels for maritime transport


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CERTH CENTRE FOR RESEARCH & TECHNOLOGY HELLAS

# Marine Fuels Decarbonization
# What Some Large Players Do

## ExxonMobil Bio Marine Fuel Oil

- FAME – VLSFO (50/50)
- 34% CO2 savings compared to conventional fossil marine fuel

## BP Marine Fuel

- FAME – LSFO (30/70)
- 26% CO2 savings compared to conventional fossil marine fuel

## Repsol

- Partnership with Navantia

## Maersk

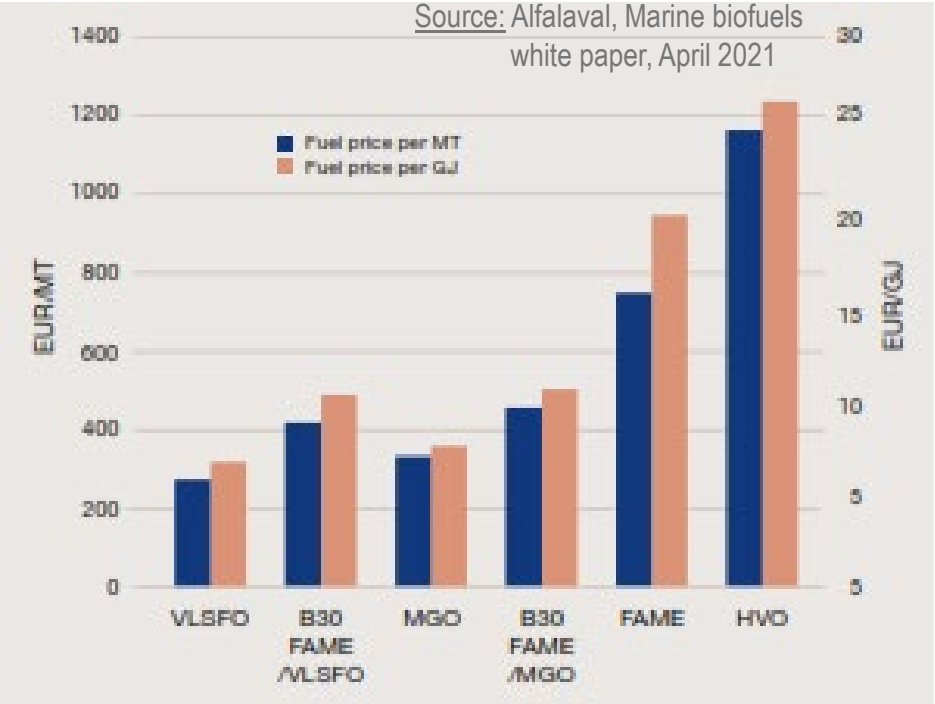
- Carbon neutral methanol

**Sustainability**

**Feedstock availability**

**Compatibility**

**Viability**




# Low Carbon Fuels @ CERTH
# Present & Future

## Track Record

- Strategic collaborations with academic institutions and industry in EU, USA and Asia
- 25 successful R&D projects funded by both the public and private sector
  - 75% EU, 25% non-EU
  - 70% public, 30% private

## Aim

- Conducting high quality research
- Employing state-of the art infrastructure (lab/pilot plants, analytical, automation and instrumentation)
- Collaborating with international industry (petrochemical, biofuels, catalyst, automotive)
- Developing synergies with top EU and USA academic/research institutions

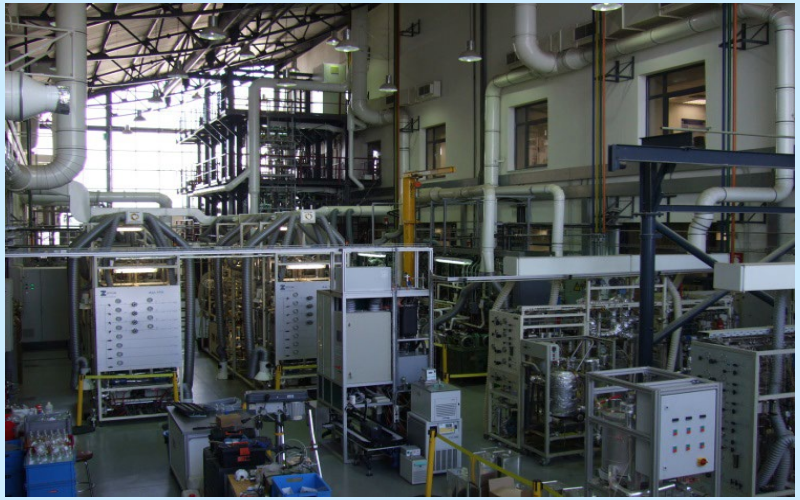
## R&D Focus

- Catalytic hydroprocessing and isomerization optimization
- Hydrothermal liquefaction for biomass depolymerization
- Lipids (plant oils, cooking oil, algal oil) upgrading to HVOs
- Pyrolysis bio-oil stabilization
- Biocrude upgrading
- Plastics-to-oil
- Co-hydroprocessing bio-based feedstocks with petroleum fractions
- Drop-in fuels (biojet, bio-diesel)
- Hybrid fuels (gasoline, jet, diesel)
- E-fuels

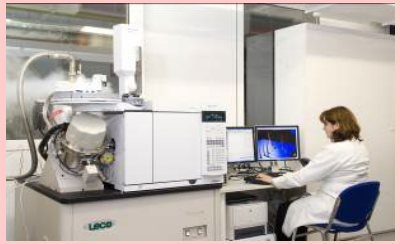
# Infrastructure

## Bench/lab scale

## Pilot Plant units



## Analytical Equipment



## General Infrastructure

# Green HVO Diesel / e-diesel Lipids Hydroconversion

- Residual / algal lipids upgrading
  - Development & demonstration of innovative HVO technology based on residual lipids (www.biofuels2g.gr)
  - Technical and environmental evaluation of residual lipids' upgrading to diesel and jet
  - Microalgal oil hydroconversion
  - Solar-based H2 employed

| | FAME biodiesel | HVO Diesel | Fossil diesel |
|---|---|---|---|
| Density (g/ml) | 0,85-0,90 | 0,79 | 0,85 |
| Cetane index | 58 | 77 | 55 |
| Viscosity@40°C (cSt) | 3,9-7,9 | 3,5 | 2,7 |
| Oxid. stability (hr) | 0,9-10 | > 22 | > 22 |
| Heating value (MJ/l) | 32,6-35,5 | 38 | 35,9 |


- Why HVO diesel?
  - Improved combustion (reduced fuel consumption less smoke, reduced noise)
  - Flexible storage / transport logistics (no bacterial growth issues, odorless)
  - Engine compatibility, drop in biofuels
  - $CO_2$ emissions reduction (low- to zero-carbon fuel)

**Selected publications**


- Waste cooking oils exploitation targeting EU 2020 diesel fuel production: Environmental and economic benefits [10.1016/j.jclepro.2019.01.211]
- Characterization of Hydroprocessed Used Cooking Oils as High Cetane Number Blending Component for Automotive Diesel [doi:10.4271/2018-01-1745]
- Animal fats valorization to green transportation fuels: From concept to industrially relevant scale validation, [ DOI: 10.1016/j.wasman.2022.03.001
- Improving PM-NOx trade-off with paraffinic fuels: A study towards diesel engine optimization with HVO, [DOI: 10.1016/j.fuel.2019.116921]


Life Eurobank ΕΣΠΑ 2014-2020 ανάπτυξη - εργασία - αλληλεγγύη

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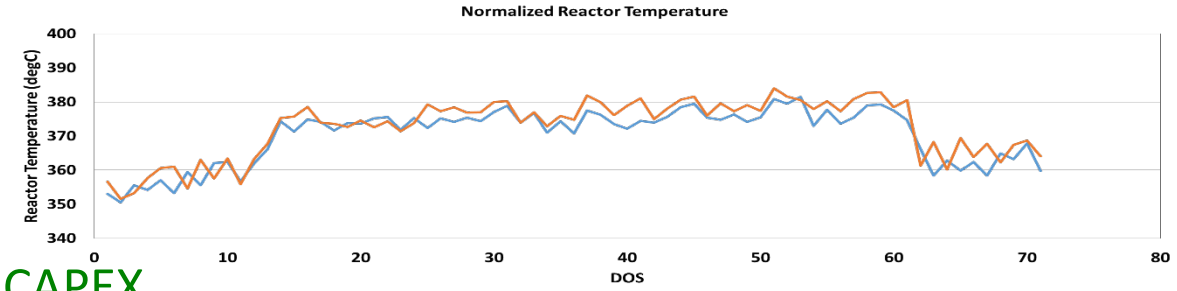
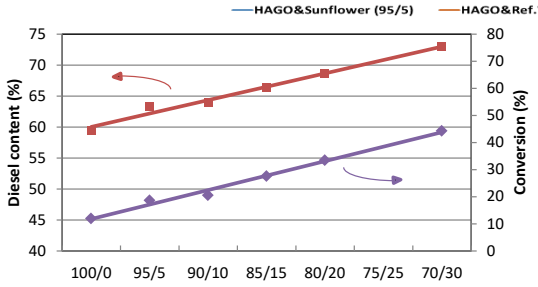
# Hybrid Fuels
# Lipids Co-processing

- Lipids integration in refineries
  - Technical and environmental evaluation of residual lipids' integration in refinery (www.sustaindiesel.gr)
  - Pre-commercial scale testing of lipids integration in refinery
  - Process intensification (max product selectivity, max bio-content, min energy/H2 requirements)
  - Reliable integration (end-fuel specifications abide standards, catalyst extended life)
- Why hybrid diesel?
  - Direct refinery $CO_2$ savings
  - Fast renewable feedstock uptake in refinery, low CAPEX
  - Engine compatibility, drop-in fuels

| Properties | Units | Hybrid diesel | Market diesel |
|---|---|---|---|
| Density | kg/m³ | 825,8 | 829,2 |
| Flash point | °C | 61 | 67 |
| Sulpur | wppm | 8,2 | 5,8 |
| Viscosity (40°C) | cSt | 2,996 | 3,066 |
| Cetane index | | 59,1 | 58,3 |
| Cetane number | | 56,7 | 55,7 |
| Water | wppm | 100 | 60 |
| CFPP | °C | -2 | 0 |
| Polyaromatics | %w/w | 1,1 | 1,4 |
| Lubricity | µm | 181 | 174 |
| Recovery 95% v/v | °C | 353 | 353,2 |
| Recovery at 250°C | %v/v | 26,8 | 25,8 |

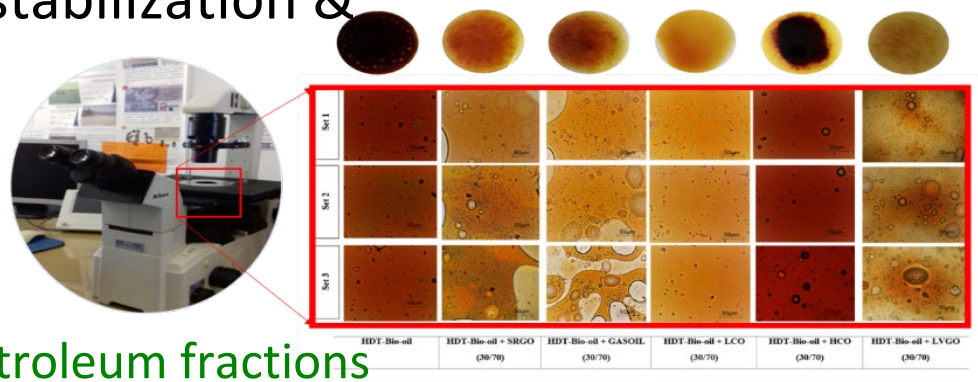




**Selected publications**

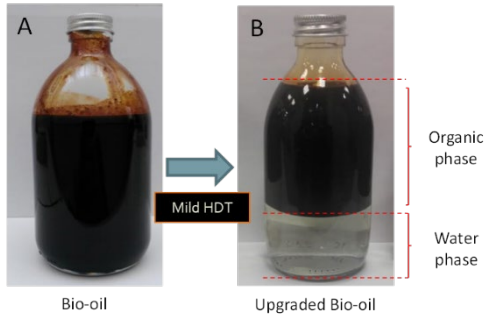
- Waste cooking oils exploitation targeting EU 2020 diesel fuel production: Environmental and economic benefits [10.1016/j.jclepro.2019.01.211]
- Effective and sustainable LCO upgrading using distillation and co-hydroprocessing with waste cooking oil [10.1016/j.fuproc.2020.106676]
- Refinery co-processing of renewable feeds [10.1016/j.pecs.2018.04.002]
- The Suspending Role of $H_2O$ and CO on Catalytic Hydrotreatment of Gas-oil; Myth or Reality? [10.1016/j.fuproc.2015.12.007]

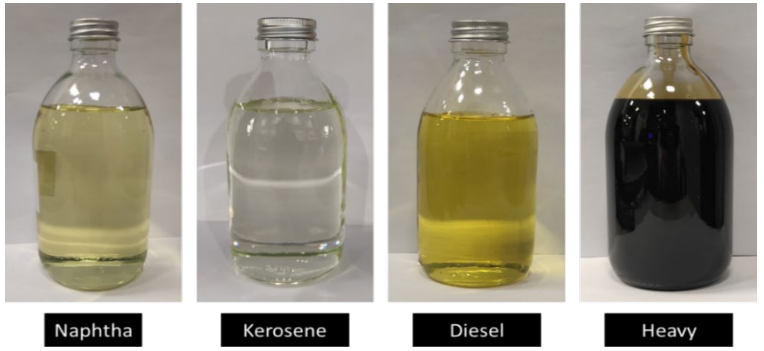
# Bio-based Intermediates
# Pyrolysis Bio-oil Co-Processing

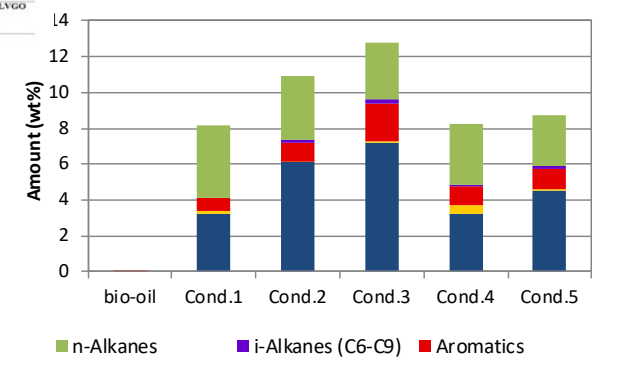
- Residual biomass pyrolysis oils stabilization & refinery integration
  - Lignin carbon conversion max
  - Catalytic system intensification via smart catalyst loading
  - Miscibility improvement with petroleum fractions
  - Stabilized pyrolysis bio-oil integration
  - in refineries (www.biomates.eu)
- Why pyrolysis-based diesel?
  - Increase biomass availability
  - Pyrolysis side-streams potentially improve economic viability
  - Direct fuels decarbonization

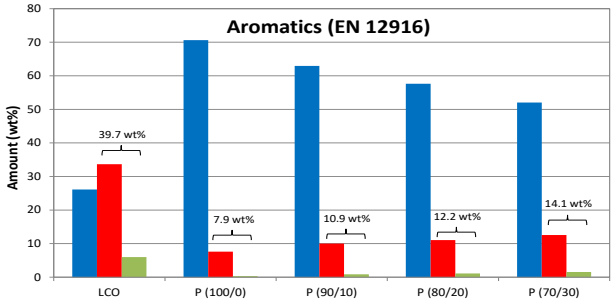



Bio-oil / Petroleum intermediates
200x



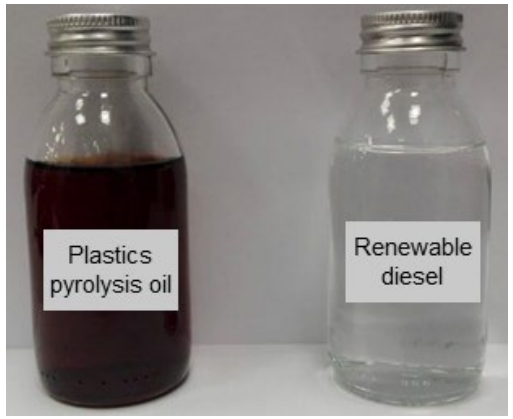




**Selected publication**

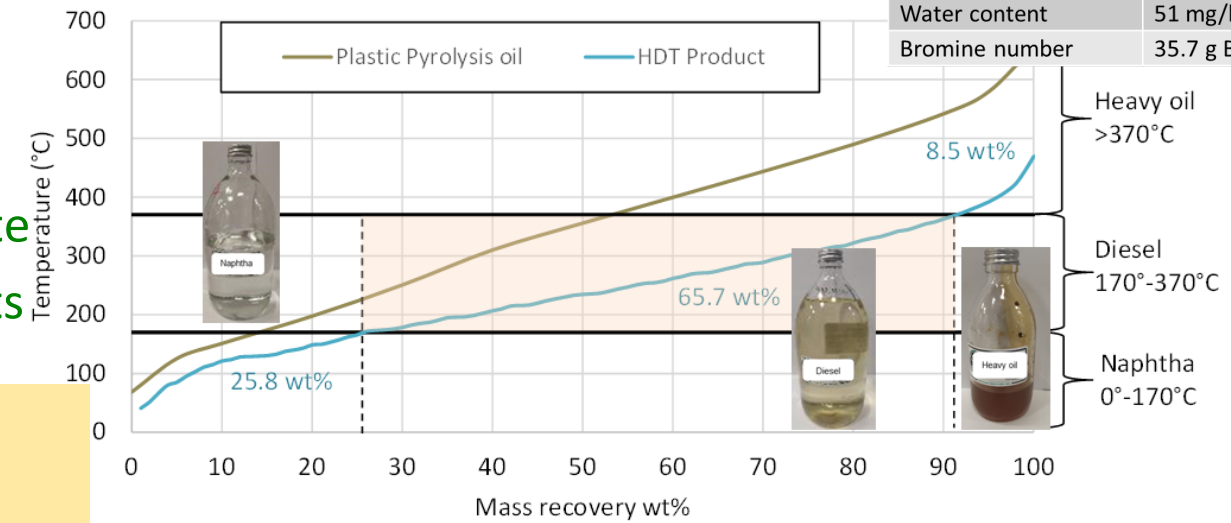

- Impact of hydrogenation on miscibility of fast pyrolysis bio-oil with refinery fractions towards bio-oil refinery integration [10.1016/j.biombioe.2021.106171]
- Bio-based refinery intermediate production via hydrodeoxygenation of fast pyrolysis bio-oil [10.1016/j.renene.2020.12.047]
- Refinery co-processing of renewable feeds [10.1016/j.pecs.2018.04.002]
- Study on phase behavior and properties of binary blends of biooil/fossil-based refinery intermediates: A step toward bio-oil refinery integration [10.1016/j.enconman.2018.01.023]


# Renewable Non-biogenic Diesel Plastics Pyoil Hydroconversion

- Plastic waste pyrolysis oil (Pyoil) upgrading and valorization
  - Development of hydroconversion protocol of PyOil
    - » Crude Pyoil, diesel fraction of Pyoil
  - Catalytic system assessment, multiple hydroprocessing steps evaluation
  - Hydroconversion limitations and potential
- Why Plastics Pyoil diesel?
  - Direct recycling problematic waste
  - Reduced conversion requirements compared to biomass




| Property | Mid-distillate PyOil fraction | Diesel product |
|---|---|---|
| Density (@15°C) | 802.7 kg/m³ | 790.6 kg/m³ |
| Viscosity (@40°C) | 2.300 mm²/s | 2.377 mm²/s |
| Sulfur (wppm) | 42.9 mg/kg | 12.1 mg/kg |
| Mono-aromatics | 7.7 wt% | 1.8 wt% |
| Di-aromatics | 1.9 wt% | - |
| Tri+-aromatics | 0.4 wt% | - |
| Recovered @250°C | 36.3 vol% | 41.0 vol% |
| Recovered @350°C | 93.8 vol% | 95.2 vol% |
| Derived Cetane # | 60.7 | 74.7 |
| Flash point | 48.0°C | 52.5°C |
| CFPP | -1°C | 2°C |
| Oxidation stability | 49 g/m³ | 2.1 g/m³ |
| Water content | 51 mg/kg | 40 mg/kg |
| Bromine number | 35.7 g Br/100 gr | <0.1 g Br/100 gr |

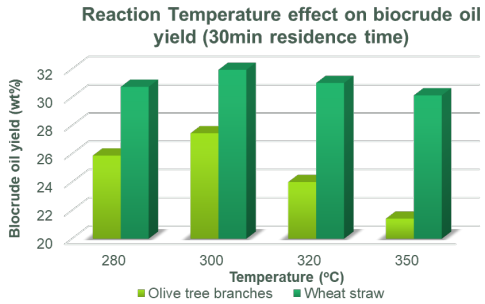


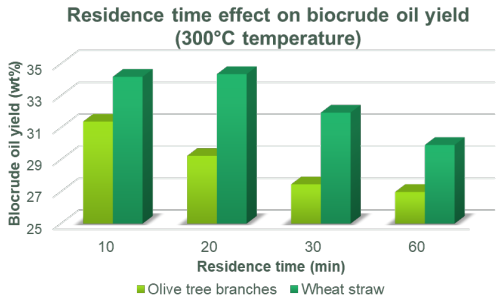

**Selected publications**

- Renewable Diesel from Waste Plastics [10.3390/en10111750]
- Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review [10.1016/j.rser.2016.09.120]

# Biomass Depolymerization
# Hydrothermal Liquefaction Biocrude

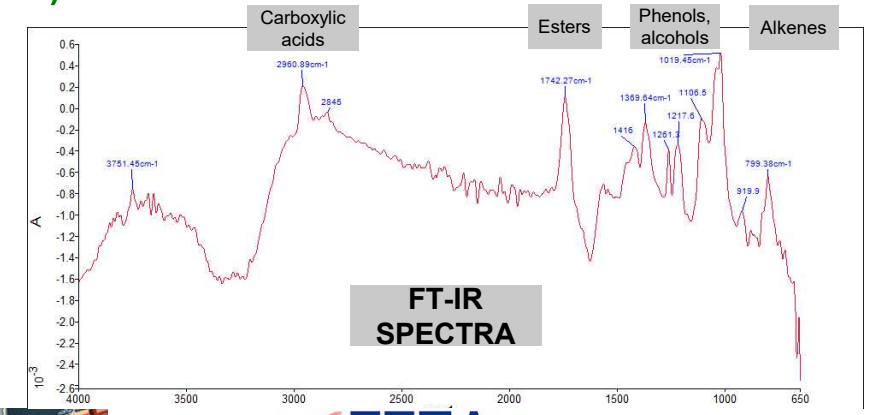
- Hydrothermal liquefaction (HTL) of residual biomass/wastes towards biofuels
  - Development of HTL process for various residual feedstocks
  - Process optimization (max yield)
- Why HTL biocrude?
  - Technology compatible with high water-content feedstocks such as biomass, algal biomass, sewage sludge (no drying required)
  - Higher yields over other depolymerization technologies

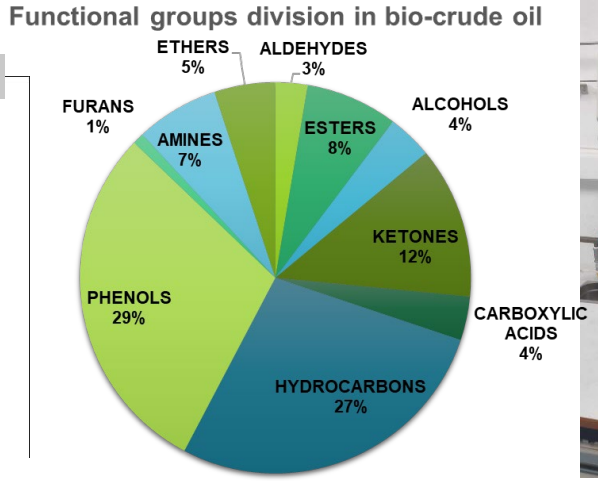



**GAS PRODUCTS**

| Chemical Compound | Concentration %v/v |
|---|---|
| Hydrogen | 0.7 – 1.8 |
| Ethane | 0 – 0.08 |
| Propane | 0 – 0.16 |
| Hydrocarbons $C_6^+$ | 0.2 – 0.35 |
| Carbon Dioxide | 97.8 - 99 |



Batch autoclave reactor

**Selected publications**

- Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review [10.1016/j.rser.2016.09.120]

# Low Carbon Fuels and Maritime Transport

- Bio-based low carbon fuels such as HVO-diesel, hybrid diesel can contribute to significant reduction of GHG emissions while respecting the IMO 2020 sulfur limits
- Non-biogenic origin diesel such as plastics pyrolysis oil can promote maritime decarbonization while promoting cyclic economy
- New emergent biofuels technologies have the potential to decarbonize faster maritime transport via more sustainable and economically viable routes

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