Postopki kemijskega recikliranja plastičnih snovi

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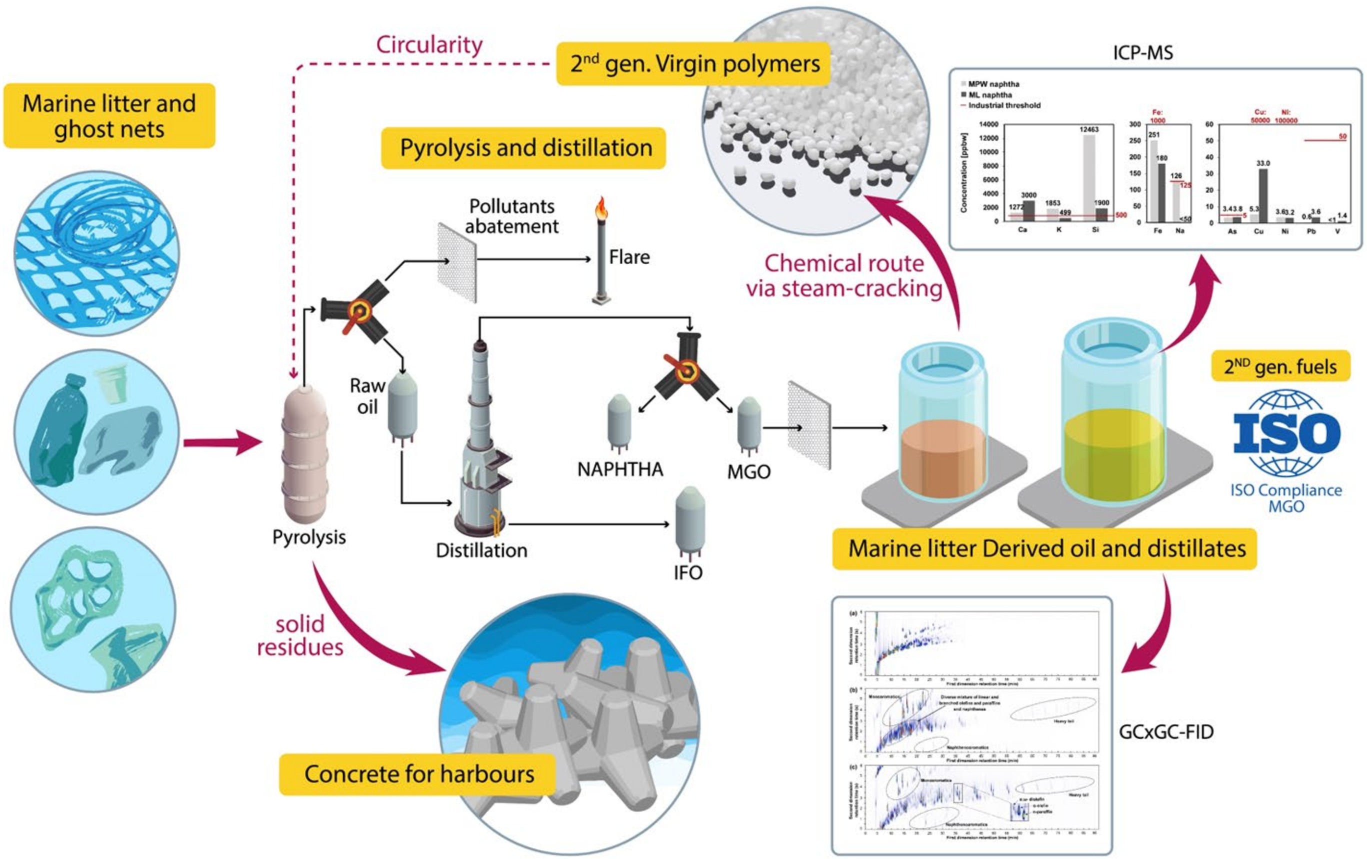

Circularity
2nd gen. Virgin polymers
ICP-MS
Marine litter and ghost nets
Pyrolysis and distillation
Pollutants abatement
Flare
Chemical route via steam-cracking
Raw oil
Pyrolysis
Distillation
NAPHTHA
MGO
IFO
2ND gen. fuels
ISO Compliance MGO
Marine litter Derived oil and distillates
solid residues
Concrete for harbours
GCxGC-FID

Feedstock

Marine Litter

Co-funded by the European Maritime and Fisheries Fund

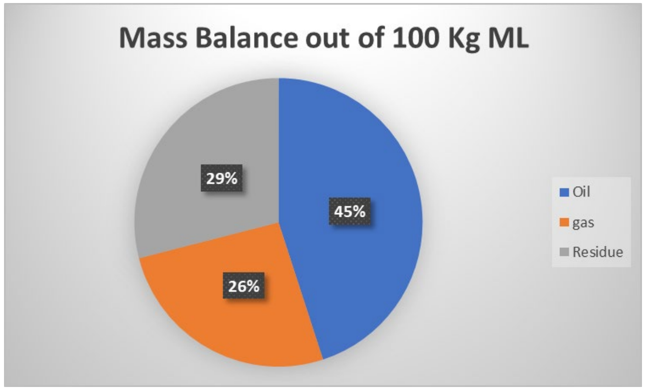
- Circularity within the Blue Economy;
- Mapping and recycling ML and ghost nets;

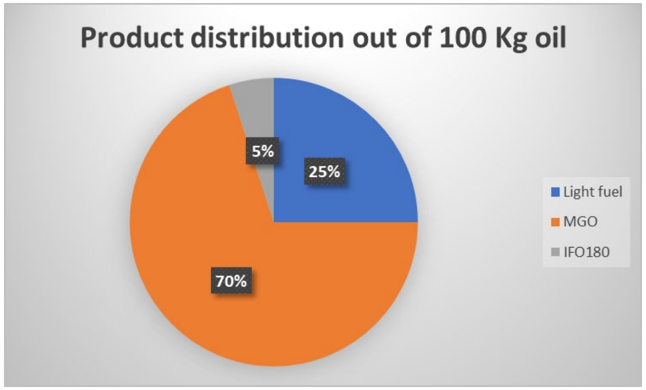
- Benthic ML (20-25 m depth);
- Polyolefins, polyesters and polyamides with some contribution of polystyrene and rubbers;
- Processed “as it is”;
- Focus on MGO for fishermen.

Actual marine litter used in pyrolysis tests: a) mixed containers, b) mussel nets, c) Eco leather, d) mooring lines, e) trawl fishing nets, f) mixed floating litter.

Pyrolysis and marine fuels

Pyrolysis/distillation results





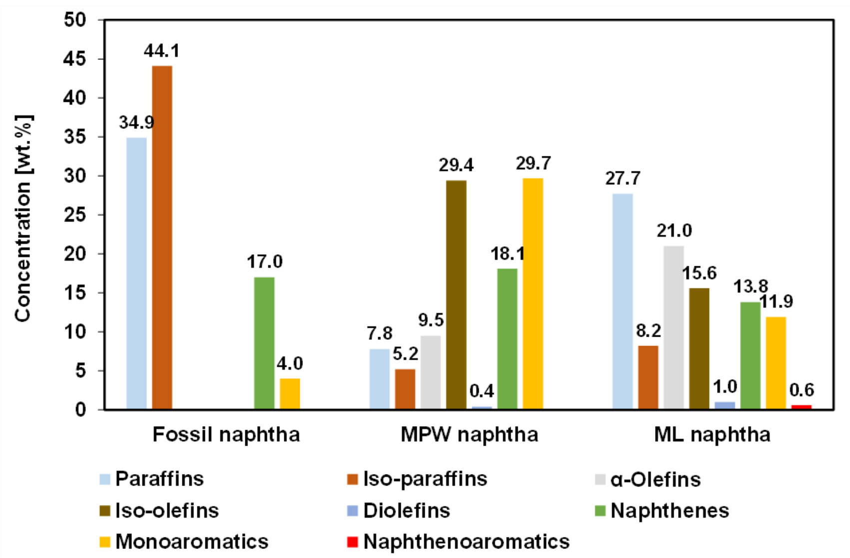
- **MGO is compliant with ISO 8217 (DMA/ULSFO)**
- Cetane index: 61,3 (target: > 45)
- S: 196 ppm (target: < 1000 – MARPOL VI ECAs)
- Pour point winter: -6 °C
- Acid number: 0,136 mg KOH/g (target: < 0,5)
- CO_2 avoidance: 0,5 tonCO_2 per ton MGO*

Visual appearance of ML naphtha (left) and MGO (right)

* Benavides et al., 2017

Steam cracking

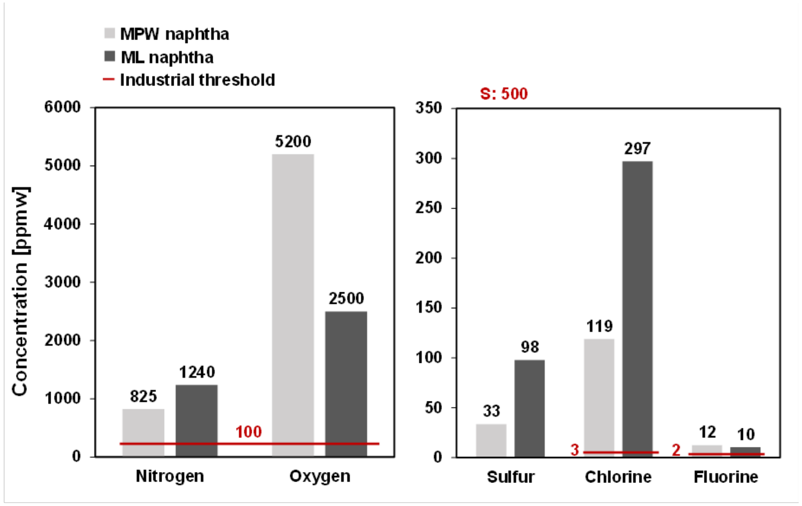
Naphthas used for Steam cracking



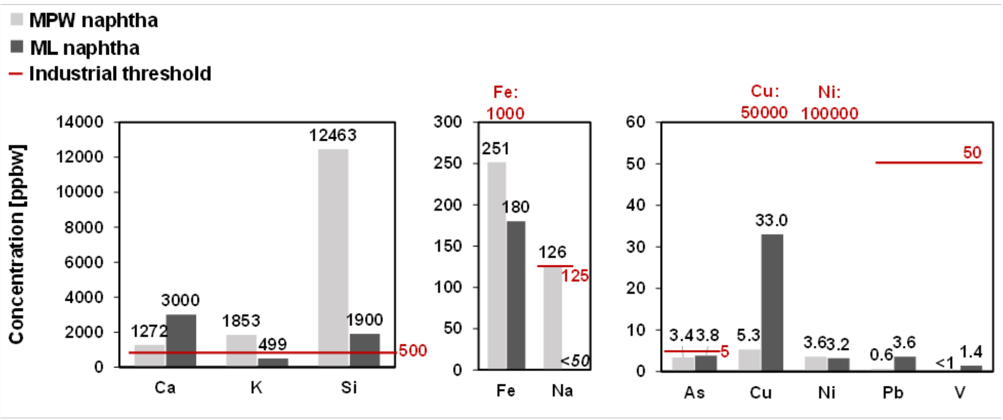
Hydrocarbon composition of the respective naphtha-range feedstocks steam cracked in this study measured using GC × GC-FID.

- **ML and MPW naphthas compared to conventional fossil naphtha**
- The high amounts of aromatics, olefins and naphthenes, as found in the two waste-derived feedstocks are likely to cause issues during steam cracking such as increased coke formation and fouling
- In both waste-derived naphtha fractions, the relative concentration of benzene (C6) is quite low, whereas the relative share of C8 aromatics (i.e., styrene, ethylbenzene, xylene) is substantial
- Aromatic removal via liquid-liquid extraction is a feasible upgrading step

Naphthas’ heteroatom analysis



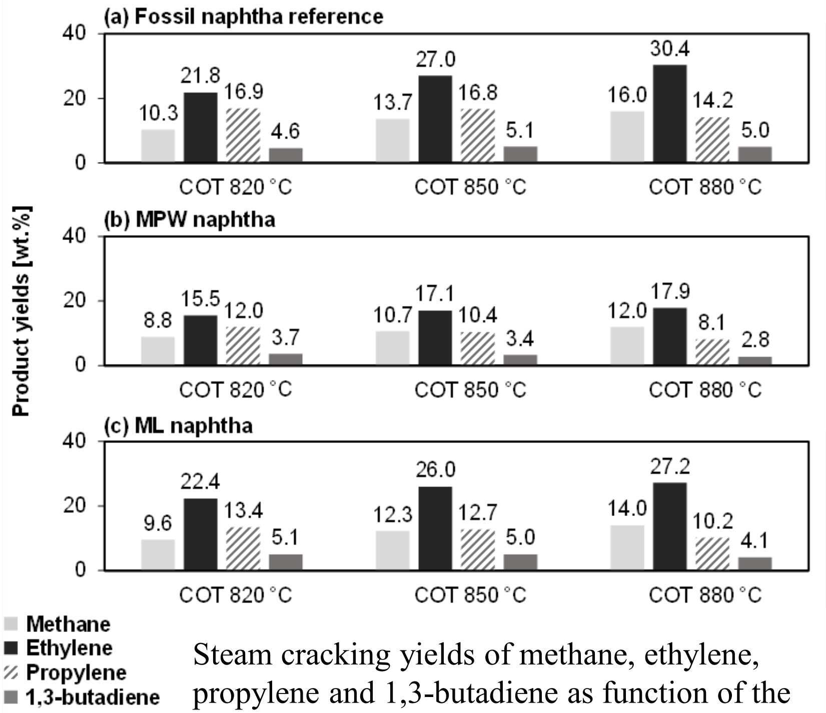
Heteroatom concentrations measured using GC × GC-SCD (sulfur) and GC × GC-NCD (nitrogen), elemental analysis (oxygen) and combustion ion chromatography (chlorine, fluorine).



Metal contaminant data compared to the known industrial threshold values.

Considering the low detection limits of ICP-MS, it is now possible to conclude that the used feedstocks comply with industrial steam cracker feedstock specifications in terms of iron, arsenic, nickel, vanadium and lead which are among the most severe poisons for downstream catalysts of steam crackers.

Steam cracking performance



Steam cracking yields of methane, ethylene, propylene and 1,3-butadiene as function of the COT

- High concentration of Iso-olefins and monoaromatics in MPW naphtha reduce product yields
- α-olefins in ML naphtha doesn't affect product yields

Coke formation

The amount of coke formed in the reactor was assessed after a consecutive steam cracking duration of 6 hours at a COT of 850 °C which is equivalent to 900 grams of feedstock per steam cracking experiment. Steam cracking of the fossil naphtha benchmark lead to a radiant coke formation of ~13 mg/h. The observed coke formation of the ML naphtha was moderately higher (~21 mg/h) and that of MPW naphtha was substantially higher (~41 mg/h).

Pollutants and char

Pyrolysis char residue

Parameter	Value	Unit
Moisture	5.6	wt%
Ash	66.3	wt%
Volatiles	15.4	wt%
LHV	10.58	MJ/Kg ss
C	31.1	wt%
H	1.1	wt%
N	0.3	wt%
S	0.6	wt%
Hg	<100	µg/Kg
Cl	1.67	wt%

Proximate analysis of ML char

- Almost all inorganics (ash);
- Volatiles arising from incomplete pyrolysis;
- Cl successfully captured as calcium chloride: but potential issue from its solubility in water. Different use of CaO envisaged.

- Stabilization with Portland cement:
  - 2 parts char;
  - 2 parts silica sand;
  - 1 part Portland cement (II/B, 32,5 R)

ML char and stabilized char

Pyrolysis char residue: leaching test

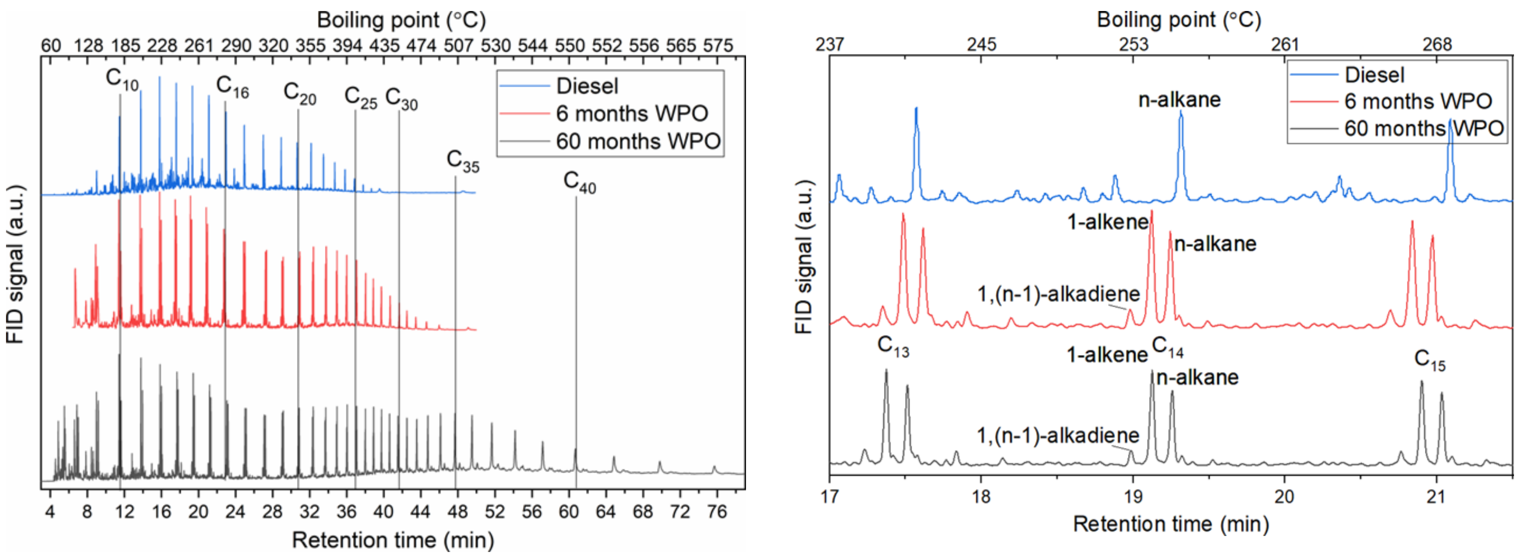
SAMPLE		Solid residue	Stabilized solid residue	Limits for recovery	Limits for disposal
PARAMETER	Unit	Value			
pH	pH		12,5	5,5-12,0	-
Conducibility @ 25°C	mS/m		828	-	-
Sb	mg/L	0,044	0,0099	-	0,07
As	mg/L	0,00081	< 0,001	0,05	0,2
Ba	mg/L	1,3	3,8	1	10
Be	mg/L		< 0,0001	0,01	-
Cd	mg/L	<0,0020	< 0,0001	0,005	0,1
Co	mg/L		0,00023	0,25	-
Cr	mg/L	0,023	0,012	0,05	1
Hg	mg/L	<0,002	< 0,0005	0,001	0,02
Mo	mg/L	0,052	0,017	-	1
Ni	mg/L	0,002	0,0057	0,01	1
Pb	mg/L	2,4	0,0047	0,05	1
Cu	mg/L	0,061	0,0066	0,05	5
Se	mg/L	0,022	< 0,001	0,01	0,05
V	mg/L		< 0,0001	0,25	-
Zn	mg/L	0,24	< 0,005	3	5
Total cyanides (CN)	mg/L		< 0,005	50	-
Chloride	mg/L	2000	320	100	2.500
Fluoride	mg/L	1,9	5,4	1,5	15
Nitrate	mg/L		< 2,0	50	-
Sulfate	mg/L	72	62	250	5.000
Asbestos	mg/L		< 1,0	30	-
Chemical oxygen demand (ST-COD)	mgO2/L		780	30	-
Dissolved organic carbon (DOC)	mg/L	590	300		100
Total dissolved solids (TDS)	mg/L		8800		10.000

- Chloride, fluoride, chemical oxygen demand and dissolved organic carbon exceed limits for recovery;
- pH probably induced by the same Portland concrete, and/or CaO addition;
- It is worth noticing that stabilization was attained using 40% residue in concrete/silica sand blend, which is a very high ratio; thus reducing the ratio to 5 – 10% should be beneficial;

- *Italian laws DM 5/2/98 all. 3 modified by DM 186 of 5/4/06 "recovery of non-hazardous waste"; and DM 27/9/2010 tab. 5 "limits for non-hazardous waste disposal"*

Combustion and ageing of waste pyrolysis oil

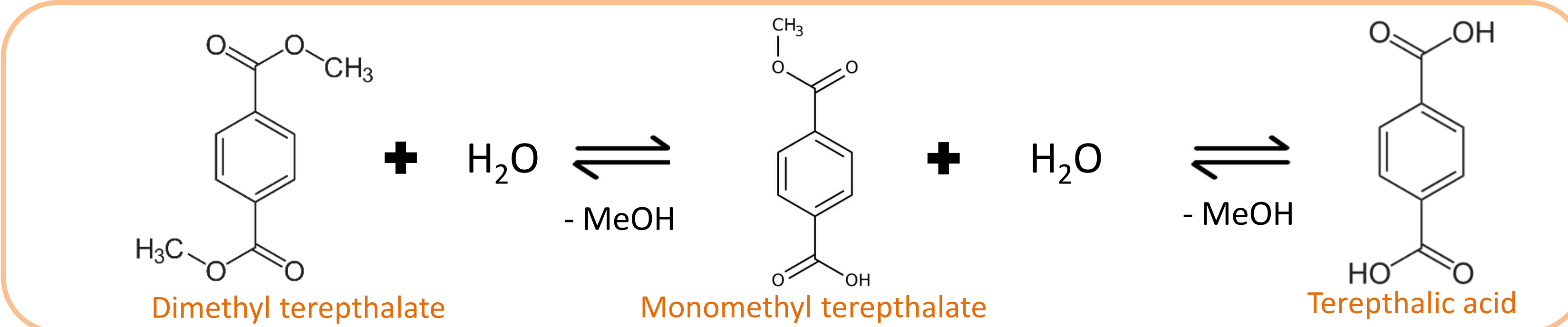
Ageing of raw pyrolysis oil



GC-MS chromatograms of diesel and aged WPO, with estimated boiling points of eluents.

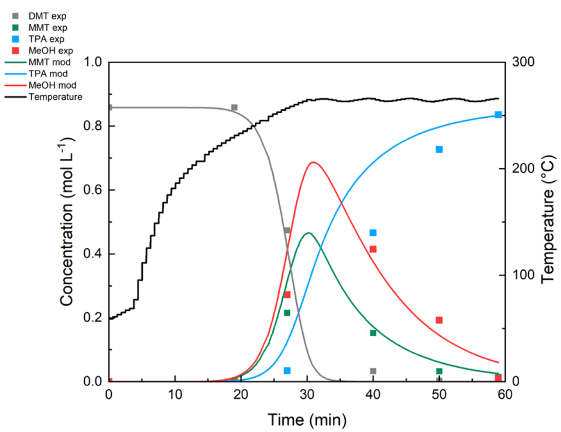
Analytical comparison between commercial diesel, a sample WPO aged for 0.5 and 5 years

Recylcing of PET from packaging



ΔT

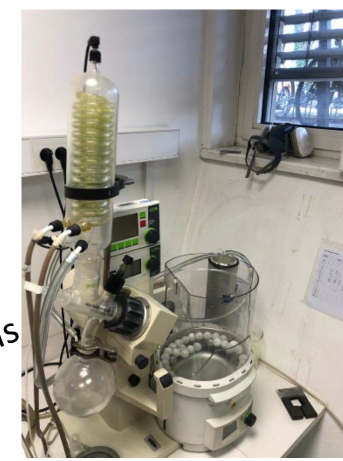
Dilution with DMSO



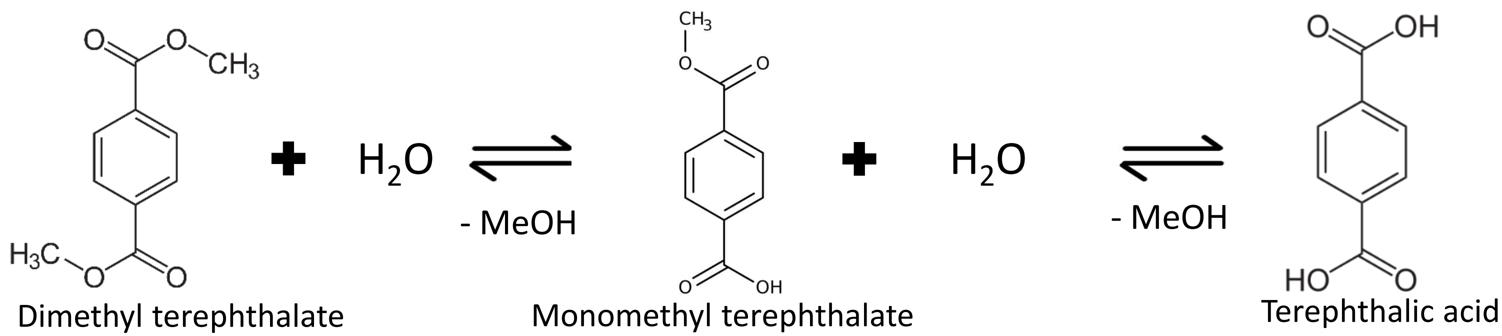
Kinetic evaluation

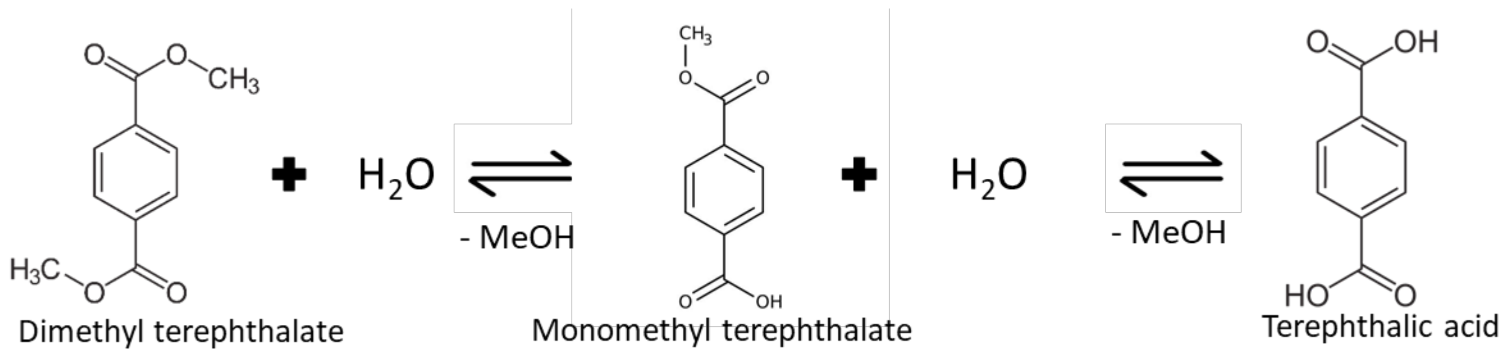
HPLC analysis

GC-MS analysis



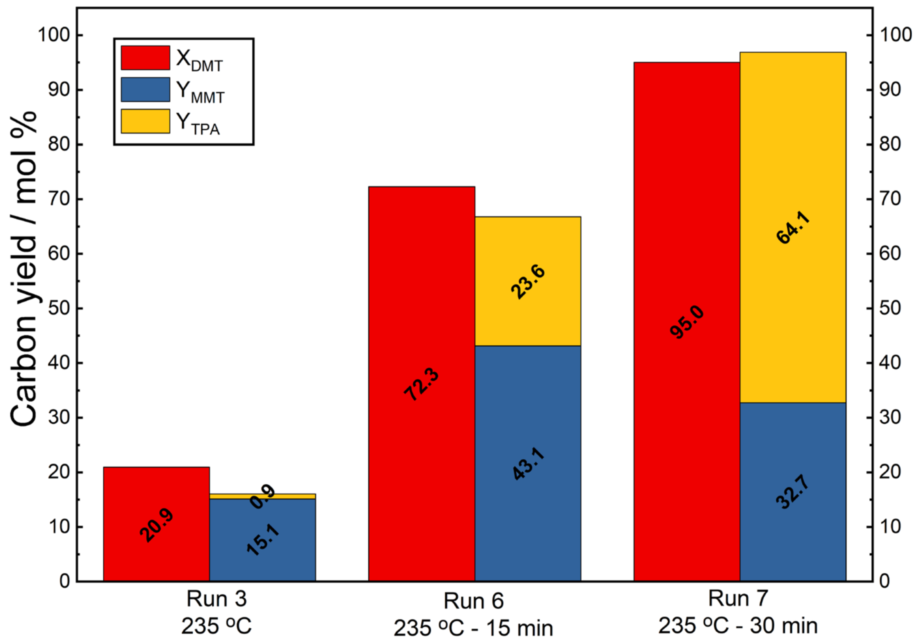
Water removal


H2O
- MeOH
H2O
- MeOH
Dimethyl terephthalate
Monomethyl terephthalate
Terephthalic acid


H2O
- MeOH
H2O
- MeOH
Dimethyl terephthalate
Monomethyl terephthalate
Terephthalic acid

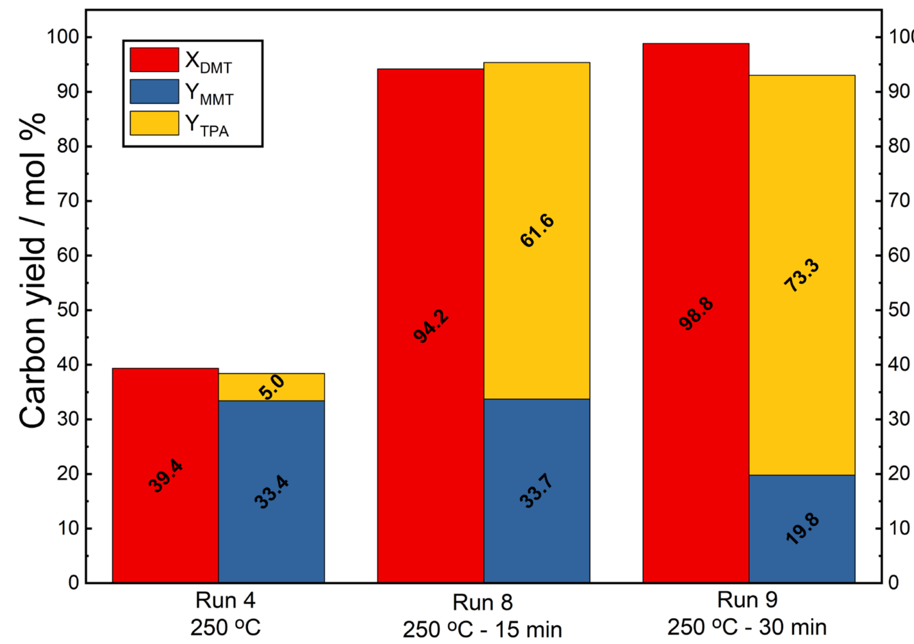
DMT hydrolysis kinetics at 235 °C

Concentrations [mol L^-1]					
Exp No.	Init. DMT	DMT	MMT	TPA	MeOH
3	0.86	0.68	0.13	0.00 8	0.086
6	0.86	0.24	0.37	0.20	0.39
7	0.86	0.04	0.28	0.55	0.68



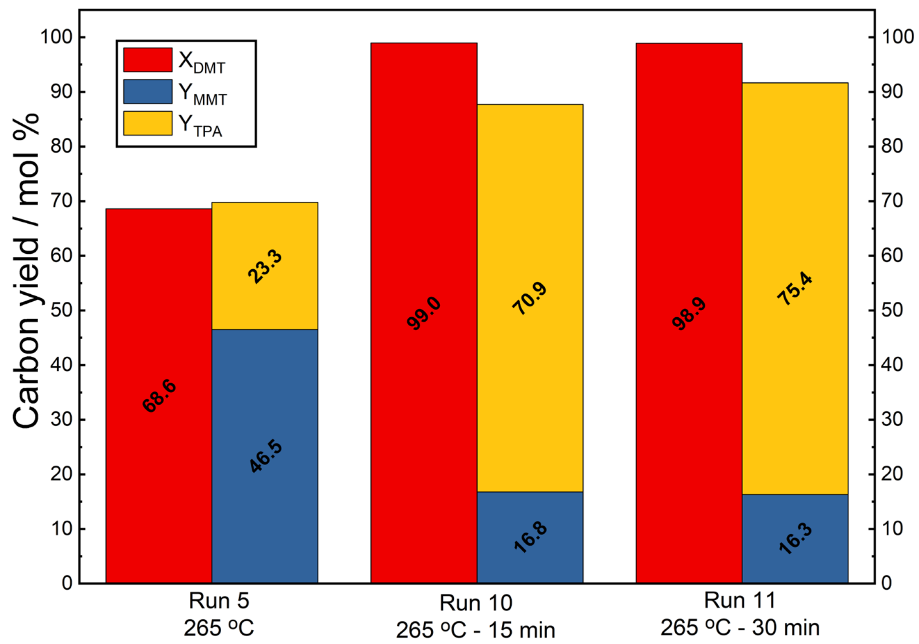
DMT hydrolysis kinetics at 250 °C

	Concentrations [mol L^{-1}]				
Exp No.	Init. DMT	DMT	MMT	TPA	MeOH
3	0.86	0.68	0.13	0.008	0.086
4	0.86	0.39	0.18	0.03	0.22
8	0.86	0.05	0.29	0.53	0.76
9	0.86	0.01	0.17	0.63	0.80

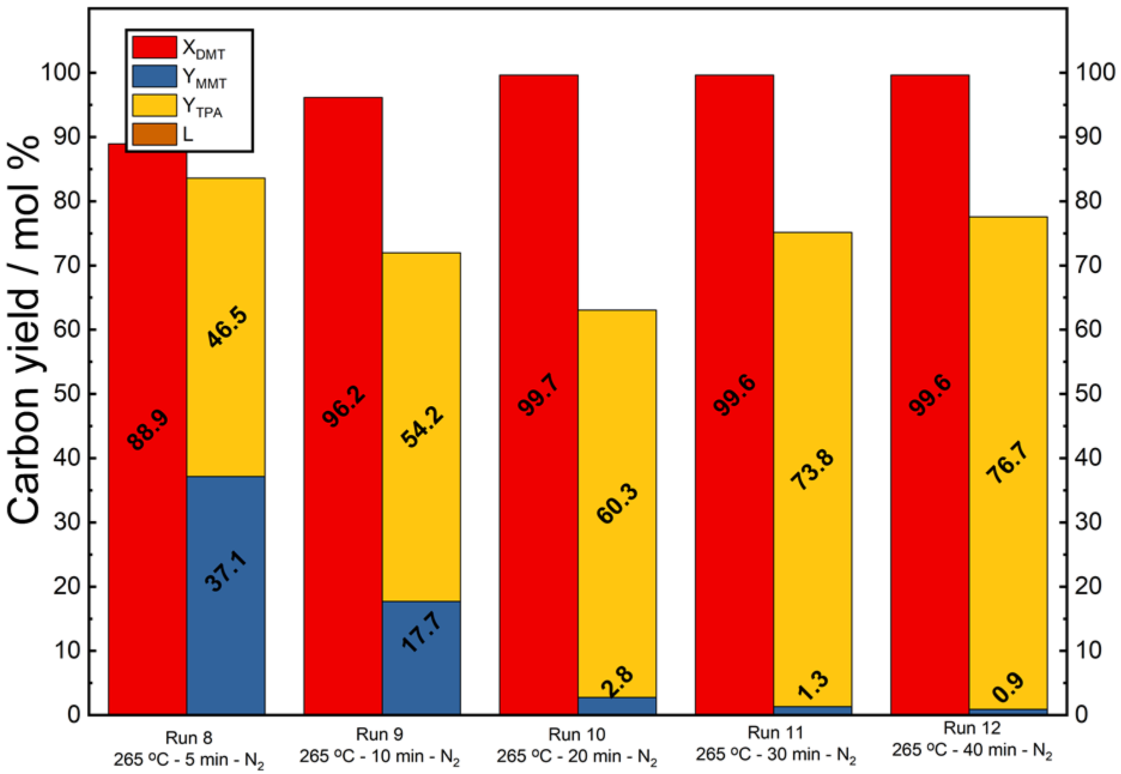


DMT hydrolysis kinetics at 265 °C

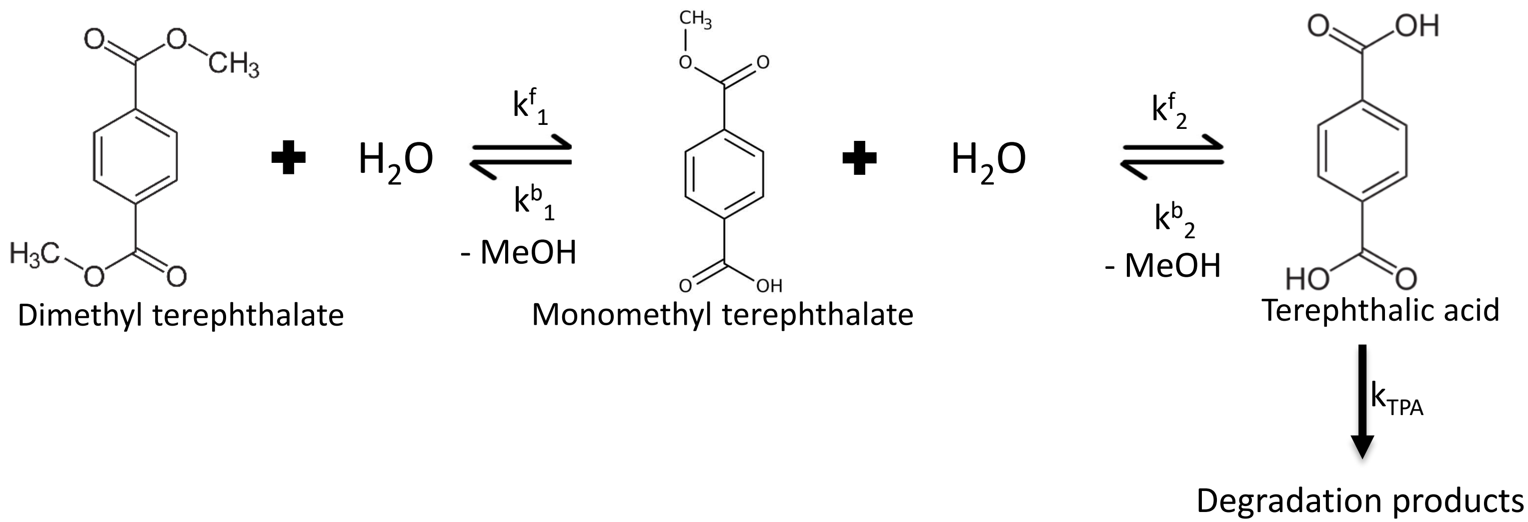
	Concentrations [mol L^{-1}]				
Exp No.	Init. DMT	DMT	MMT	TPA	MeOH
3	0.86	0.68	0.13	0.008	0.086
4	0.86	0.39	0.18	0.03	0.22
5	0.86	0.27	0.4	0.2	0.56
10	0.86	0.009	0.15	0.6	0.79
11	0.86	0.009	0.14	0.65	0.75



DMT dydrolysis with methanol removal →reflux condenser held at 90 °C



	Concentrations [mol L⁻¹]				
Exp No.	Init. DMT	DMT	MMT	TPA	MeOH
3	0.86	0.68	0.13	0.008	0.086
4	0.86	0.39	0.18	0.03	0.22
5	0.86	0.27	0.4	0.2	0.56
12	0.86	0.095	0.32	0.47	0.55
13	0.86	0.03	0.15	0.47	0.41
14	0.86	0.003	0.03	0.52	0.19
15	0.86	0.003	0.01	0.64	0.09
16	0.86	0.003	0.0077	0.66	0.06



Kinetic parameters

k_{1f} [min^{-1}]	k_{1b} [min^{-1}]	k_{2f} [min^{-1}]	k_{2b} [min^{-1}]	Ea_{1f} [$kJ\ mol^{-1}$]	Ea_{2f} [$kJ\ mol^{-1}$]	k_{TPA} [min^{-1}]	Ea_{TPA} [$kJ\ mol^{-1}$]
0.228 ± 0.017	$9.3x10^{-7}$	0.151 ± 009	0.0010 ± 0.0001	95 ± 3.2	64 ± 3.0	0.0097± 0.0008	70 ± 6

Conclusions

Conclusions

- Marine litter is a growing problem worldwide with limited remediation instruments;
- 100 kg of actual marine litter, including fishing nets, was processed "as it is" by means of pyrolysis and successfully largely converted, approximately 51% (V/V), to marine gasoil (MGO) compliant with ISO8217 DMA;
- A deep analysis of the chemical composition of pyrolysis oil and its distillates finally revealed their peculiar chemical fingerprints: 2,4-dimethyl-1-heptene can be considered the chemical signature;
- A significant amount of valuable aromatics suggest that ML naphtha might be considered an interesting not-for-fuel hydrocarbon feedstock;
- Two naphtha-range feedstocks have steam cracked in a continuous unit in order to assess the product yields and coke formation compared with a fossil naphtha reference feedstock and ML naphtha performed well;
- Pyrolysis' gaseous emissions can be curbed to safe levels;
- Solid residues can potentially be used as filler in concrete manufacturing or disposed;
- Fresh and aged WPO were evaluated as energy carriers in IC engines.

Thank you for the attention

https://www.euronews.com/green/2020/10/21/the-dangers-of-marine-litter-and-the-innovative-methods-to-combat-it

"Sewage Surfer" of Justin Hofman, Wildlife Photographer of the Year 2017