Advanced electrified marine fuel production via hydrotreatment of plastic pyrolysis oil

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Solid plastic wastes represent an abundant cost-competitive domestic feedstock for the production of future renewable fuels. This research focuses on developing an efficient technology to convert plastic wastes into renewable marine fuels through a sustainable process, supporting the decarbonization of the shipping industry. Plastic is among the most widely used materials globally, with production steadily increasing. Out of an estimated annual global plastic production of approximately 368 million tons, Europe alone contributed around 57.9 million tons in 2019 [1]. A significant portion of this plastic ends up in soil, posing serious environmental risks. Project "Plastic2Fuels" target to process plastic wastes via pyrolysis and hydrogenolysis producing a green crude oil, that will be subsequently upgraded via catalytic hydrotreatment, rendering marine electrified fuels. The aim of the current manuscript is to present the last part of the Project, the catalytic hydrotreatment utilizing solar power hydrogen. to produce electrified marine fuel from plastic wastes pyrolysis oil.
For the purpose of the current study, a plastic pyrolysis oil obtained from the pyrolysis of municipal plastic wastes was explored. To that aim commercial hydrotreating, hydrocracking and isomerization catalysts were loaded in a small scale TRL3 hydrotreatment (HDT) pilot plant of CERTH. The main objective was to investigate the effect of the operating parameters (temperature, pressure, LHSV and H_2/pyrolysis oil ratio) in terms of product yields and quality. As a result, 5 operating conditions were tested as presented in Table 1.

Table 1 Operating parameters examined for each feedstock

Parameters	**Units**	**Condition 1**	**Condition 2**	**Condition 3**	**Condition 4**	**Condition 5**
Pressure	psi	1200	1200	1200	1500	1200
Temperature	°C	Aver. 338	Aver. 366	Aver. 366	Aver. 366	Aver. 366
H2/oil ratio	scfb	5000	5000	5000	5000	3000
LHSV	hr^{-1}	1	1	0.75	0.75	0.75

The initial plastic pyrolysis oil consisted mostly of 50.8 wt% olefins, 36.6 wt% N-paraffins, 6.2 wt% Naphthene and 3.7 wt% aromatics, however after the hydrotreatment upgrading the final liquid product was a blend consisted mostly of of N-paraffins, (56.3 – 71.7), Iso-paraffins (8.5-20.0 wt%), Naphthene (11.6-14.3 wt%) the distribution of which depended on the operating conditions. The results show that the hydrotreatment was able to transform the high olefinic content of the raw plastic pyrolysis oil to the corresponding n-paraffins and iso-paraffins.
From the five operating conditions that were investigated, the optimum condition is cond. No. 2 as high percent of paraffins and iso-paraffins were produced with an average hydrogen consumption. At the next step the process was scaled-up on a TRL 5 hydrotreatment plant for the validation and demonstration of the technology. The total organic liquid product produced on the TRL 5 HDT plant was fractionated in a batch fractionation unit at CERTH, leading to the production of 25 L of advanced electrified marine fuel and 16 L of an electrified advanced heavy heating oil. The properties of the produced marine fuel, heating oil and DMA specifications for the marine diesel are presented in Table 2. The produced advanced electrified marine fuel not only fulfils all DMA specifications for marine diesel but it is even better in some properties. More specifically, the cetane index is really high for the produced fuel (69.89) compared to the lower limit of DMA (>40) providing better efficiency during its combustion on internal combustion diesel engines. In addition, the sulphur content is very low (15.3 wppm) given an advantage in terms of sustainability and environmental emissions during its combustion. The flash point is very high (93 °C) compared to the lower limit of DMA (>60°C) which shows the advantage of this fuel during storage and handling as it indicates how easily the fuel can ignite under normal handling and storage conditions. In general, the produced advanced electrified marine fuel is a high-quality marine diesel that can be used either as an alternative marine diesel to commercial diesel or as a drop-in fuel to the commercial marine diesel improving in that way some of the marine fuel properties like the cetane index, the flash point and the sulphur content. To conclude, the Technology was developed and optimized successfully in a TRL 3 HDT plant while the validation and demonstration of the suggested technological pathway on the TRL 5 HDT plant has led to the production of 25 L of a high quality advanced electrified marine fuel. The residual of the process, could be potentially used as an electrified heating oil.

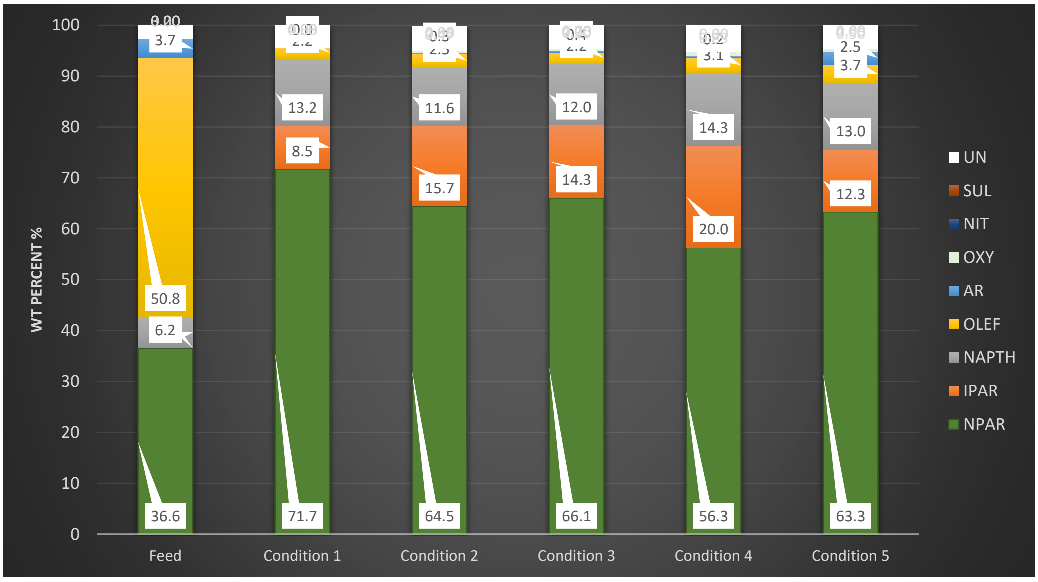

Figure 1 presents the GC analysis from the plastic waste pyrolysis oil (feed) and the products from the 5 conditions

Table 2 Properties of marine diesel and heating oil

Parameters	**Units**	**Marine diesel**	**Heating fuel**	**DMA specs**
Density at 15°C	g/ml	0.793	0.822	<0.890
S content	wppm	15.3	2.64	<1000
H content	wt%	14.66	-	-
C content	wt%	85.06	-	-
O content	wt%	0.27	-	-
N content	wt%	0.4	-	-
TAN	mgKOH/g	0	-	<0.5
Viscosity at 40°C	cSt	2.602	9.264	2.0-6.00
Flash point	°C	93	-	>60
Poor point	°C	-6	-	
Cetane index	-	69.89	-	>40
Oxidation stability	hr	>27	-	-
CFPP	°C	-6	-	-
Water (K-F)	wt%	0.002	-	-
HHV	MJ/kg	46.933	-	-

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