Plastic wastes to green transportation fuels

A. Dimitriadis[1], G. Meletidis[1], G.C. Faussone[2], D. Karonis[3], A. Odjo[4], S. Bezergianni[1]

[1]Centre for Research & Technology Hellas (CERTH), Chemical Process & Energy Resources Institute (CPERI), Thessaloniki, Harilaou-Thermi road, 57001, Greece
[2]INSER SpA, Turin, Italy
[3]School of Chemical Engineering, National Technical University of Athens, Athens 15780, Greece;
[4]Clean Planet Energy (CPE), London, UK
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Presenting author email: adimitr@cperi.certh.gr

The use of plastics has been associated with significant environmental problems due to their continuous accumulation in landfills, as plastic waste does not degrade or degrades at a very low pace. According to the World Bank (Hoornweg 2017), plastic waste accounts for 8–12% of the total municipal solid waste (MSW) worldwide, while it is estimated to increase 9-13% of MSW by 2025. The current study targets to evaluate by technical viewpoint the potential to convert waste plastics to renewable diesel fuel by an optimal combination of pyrolysis and catalytic hydrotreatment. To that purpose, mixed waste plastic mined from the old landfill was used without any pre-treatment except mechanical soil removal by a rotary screen. The plastic wastes sorted by an old landfill operating in South East Asia in 2015 and were pyrolized in a pyrolysis plant aiming pyrolysis bio-oil production.

The total pyrolysis oil produced included a wide boiling-point range of molecules that cover all transportation fuel standards (naphtha, kerosene, diesel, heavy oil). The properties and distillation characteristics of the pyrolysis oil are given in Table 1 below. According to the density (test method ASTM D4052) and distillation (test method D86), the total pyrolysis oil can render various transportation fuel products, namely naphtha, diesel and wax, of different boiling point range. More specifically, the main product is in the diesel range, attributed to 68.5%wt of the total pyrolysis oil produced. A significant product is also naphtha (gasoline), accounting for 26.5% wt of the pyrolysis oil, while there is a small yield of wax (4% wt).

Table 1 Pyrolysis oil analysis

Property	Value	Notes
°API	46.3	
Density	796.0 kg/m^3	
0 % recovered (IBP*)	82.0 °C	
30 % recovered	177.5 °C	T 170 @ 26.5%
50 % recovered	244.5 °C	
90 % recovered	372.5 °C	T 370 @ 96%
98% recovered (EP**)		
Light liquid fraction (0-170 °C)	26.5% wt	Naphtha
Medium liquid fraction (170-370 °C)	68.5% wt	Diesel
Heavy liquid fraction (>370 °C)	4% wt	Wax

*Initial boiling point
**End point

As it was aforementioned, the pyrolysis oil can be valorized better if fractionated into separate products with different boiling point ranges. The main fraction is the mid-distillate fraction (170-370 °C) accounting for 68.5%wt of the total pyrolysis oil. This fraction was separated via distillation and it was further examined as a potential diesel fuel. However, the problematic properties of this fraction, which include high sulfur content, low flash point and high oxidation stability, render this feed inappropriate as a transportation fuel without further upgrading. In order to overcome these limitations, an additional catalytic hydrotreatment step was considered.

Catalytic hydrotreatment of the mid-distillate fraction of pyrolysis oil was conducted in CERTH's hydrprocessing pilot plant. The mass balance of catalytic hydrotreating of the mid-distillate fraction of the pyrolysis oil is shown in Figure 1, while the mass balance closure was 98.8%. The conversion yield was 98.3 % wt and the H_2 consumption was 0.01 g H_2/g mid-distillate pyrolysis oil converted.

The diesel fuel produced from upgrading the mid-distillate pyrolysis oil fraction during the experimental testing at CERTH was a clear fuel (Picture 1) with average sulfur 12.1 mg/kg (see table 2). The improvement of both the appearance and sulfur content of the produced fuel was very promising and leads to the further evaluation of the fuel as a potential transportation diesel fuel.

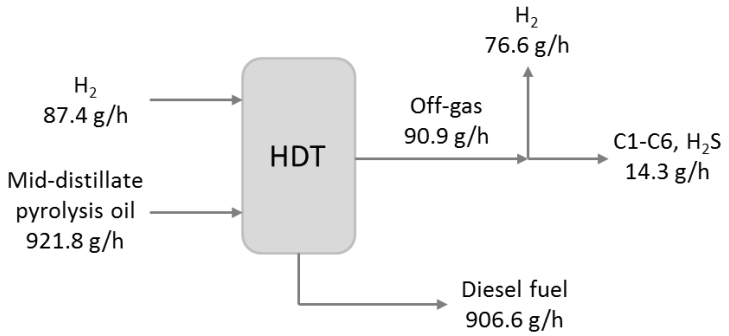
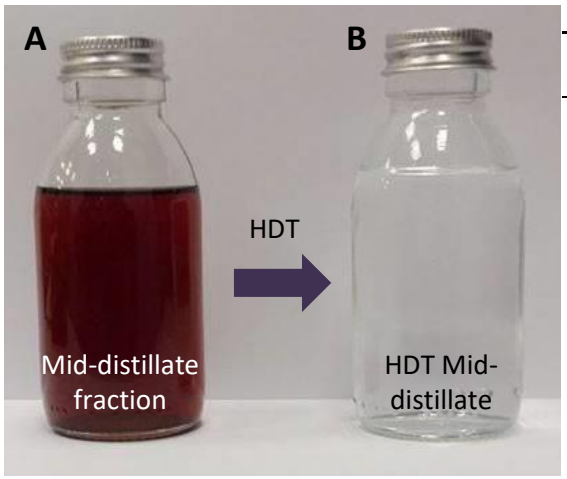


Figure 1 Mass balance of catalytic hydrotreatment (HDT) of mid-distillate pyrolysis oil fraction as estimated from the hydrotreating experiments at CERTH



Picture 1 Mid-distillate fraction of waste plastics pyrolysis oil before (A) and after (B) catalytic hydrotreatment (HDT) upgrading at CERTH

Table 2 Analysis of the hydroprocessed mid-distillate fraction of pyrolysis oil

Property	**Value**	**Unit**
Density at 15 °C	790.6	kg/m^3
Viscosity at 40 °C	2.377	mm^2/s
Sulfur Content	12.1	mg/kg
Distillation		
Recovered at 250 °C	41.0	% vol
Recovered at 350 °C	95.2	% vol
95% (V/V) Recovered at	349.5	°C
Cetane Index	71.5	
Flash Point	52.5	°C
CFPP	2	°C
Water Content	40	mg/kg
Oxidation Stability	2.1	g/m^3
Carbon Content	85,14	% wt
Hydrogen Content	14,85	% wt
Calorific value Gross	46,98	MJ/kg

The results of the analysis of the final product are given in Table 2. The hydroprocessed fuel has excellent cetane index that approaches 71.5. Density and viscosity have been slightly decreased. The proposed methodology renders a promising alternative diesel fuel. In particular, the hydroprocessed mid-distillate fraction of the pyrolysis oil is an excellent ignition quality mid-distillate fuel that in most cases meets the requirements of EN 590 standard for automotive diesel, and can be considered as a promising alternative diesel pool component. The successful conversion of the plastic waste into diesel via the proposed two-step process is attributed primarily to the improved quality of the intermediate pyrolysis oil and its mid-distillate fraction, and particularly the low density and viscosity, as well as low sulfur, water and metals content. The plastic waste pyrolysis oil properties are superior over the biomass pyrolysis oil (bio-oil), which is characterized by high water content and highly acidic (Zhang 2013) and over the scrap tire pyrolysis oil (STPO) which has high sulfur, nitrogen and metals (Na, Ca, Ti, Fe, Cu, Al, Zn, Pb, Cr) content (Pilusa 2013). As a result, the waste pyrolysis oil upgrading requires a single hydroprocessing step, while the other types of pyrolysis oil require multiple hydroprocessing steps rendering the upgrading cost unattractive as it constitutes of 70-85% of the overall production cost.

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