Article

Alternative Diesel from Waste Plastics

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Abstract: The long term ambition of energy security and solidarity, coupled with the environmental concerns of problematic waste accumulation, is addressed via the proposed waste-to-fuel technology. Plastic waste is converted into automotive diesel fuel via a two-step thermochemical process based on pyrolysis and hydrotreatment. Plastic waste was pyrolyzed in a South East Asia plant rendering pyrolysis oil, which mostly consisted of middle-distillate (naphtha and diesel) hydrocarbons. The diesel fraction (170–370 °C) was fractionated, and its further upgrade was assessed in a hydroprocessing pilot plant at the Centre for Research and Technology Hellas (CERTH) in Greece. The final fuel was evaluated with respect to the diesel fuel quality specifications EN 590, which characterized it as a promising alternative diesel pool component with excellent ignition quality characteristics and low back end volatility.

Keywords: waste plastics; pyrolysis; hydrotreating; fuels; renewable diesel; waste-to-fuel

1. Introduction

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. On average, 50% of the waste plastic generated in Europe is recovered, while the rest is sent to landfills [1]. In 2015, global plastic production reached 322 million tonnes, a dramatic increase compared to the 279 million tonnes produced in 2011 [2]. According to the World Bank [3], plastic waste accounts for 8–12% of the total municipal solid waste (MSW) worldwide, while it is estimated to increase to 9–13% of the MSW by 2025. The increasing availability of such waste material in local communities, coupled with the high energy density, render waste plastics one of the most promising resources for fuel production [4].

The pyrolysis of plastics and other MSW (end-of-life tires, organic wastes, etc.) for fuel production is practiced by several small-size companies worldwide, especially those of emerging economies, where industries such as cement, glass, and other energy-intensive sectors represent the reference market for this type of fuel (diesel-range hydrocarbons produced via the pyrolysis of plastics and MSW). The pyrolysis of plastics yields on average 45–50% of oil, 35–40% of gases, and 10–20% of tar [1], depending on the pyrolysis technology. According to previous research, there are some cases where a high amount of liquid yield, more than 80 wt %, could be produced in the pyrolysis of individual plastic, which is higher than the pyrolysis of wood-based biomass in general [5,6]. The pyrolysis oil can be valorized better if separated into separate fractions with different boiling point ranges, e.g., light (0–170 °C), mid-distillate (170–370 °C), and heavy (>370 °C) fractions. The total pyrolysis oil or fractions of it can be further upgraded via suitable conversion processes, such as catalytic

hydrotreatment, to meet market fuel standards. A two-stage pyrolysis-catalysis of high-density polyethylene has been investigated, with the pyrolysis of the plastic in the first stage followed by the catalysis of the evolved hydrocarbon pyrolysis gases in the second stage leading to gasoline range hydrocarbon oil (C8–C12), by Ratnasari et al. [7]. The results showed that, using the staged catalysis, a high yield of oil product (83.15 wt %) was obtained from high-density polyethylene. In the last years, the use of pyrolysis oil as a diesel fuel has been of main importance, and there are some latest references where they study the potential of using oils that have been derived from the pyrolysis of plastics at different temperatures in diesel engines [8]. Their results have shown that a further upgrade of pyrolysis oil is necessary in order for it to be suitable as a diesel substitute due to its unfavorable properties.

Considering all of the above reasons, the aim of this study is the technical evaluation of the potential to convert waste plastics to high-quality diesel fuel by an optimal combination of pyrolysis and catalytic hydrotreatment. The pyrolysis was performed in a semi-continuous plant in South East Asia with a 5 t/d capacity, which is located nearby an old landfill that was supplying the plant with waste plastics. The upgrading of the pyrolysis oil was tested in the hydrotreatment pilot plant of the Centre for Research and Technology Hellas (CERTH) in Greece, rendering the desired diesel fuel. The analysis of the final diesel fuel was conducted in the Laboratory of Fuels Technology and Lubricants of the National Technical University of Athens in Greece.

2. Results and Discussion

The two-step process for converting waste plastics to diesel fuel has been experimentally tested and assessed with respect to final fuel yield quality. In the sections that follow, the experimental results of the waste plastic pyrolysis and subsequent catalytic hydrotreatment are described as the outcome of the proposed waste-to-fuel pathway.

2.1. Upgrading of Plastic Waste via Pyrolysis

The plastic waste pyrolysis was produced at the semi-continuous operating pyrolysis plant in South East Asia (Figure 1). Mixed waste plastic mined from an old landfill was used without any pretreatment except for mechanical soil removal by a rotary screen. The most relevant components of plastic waste feedstock are 60–70 wt % polyethylene (PE)+polypropylene (PP) and 30–40 wt % polyethylene-terephthalate (PET). Pyrolysis was performed at approximately 400 °C and atmospheric pressure. The oil yield over the dry feedstock mass was estimated to be 49%, with an energy recovery in oil of about 54% (feedstock's Gross Calorific Value or GCV 42 MJ/kg; oil's GCV 46 MJ/kg). The feedstock had approximately 11 wt % solid residue, which in some rare cases could reach as high as 20 wt %. The overall mass and energy balance is shown in Figure 2.
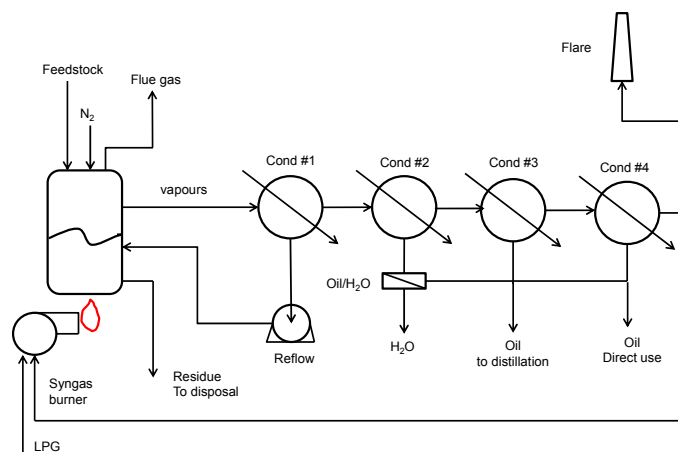

Figure 1. Simplified process flow diagram of the pyrolysis plant. LPG: Liquefied Petroleum Gas.
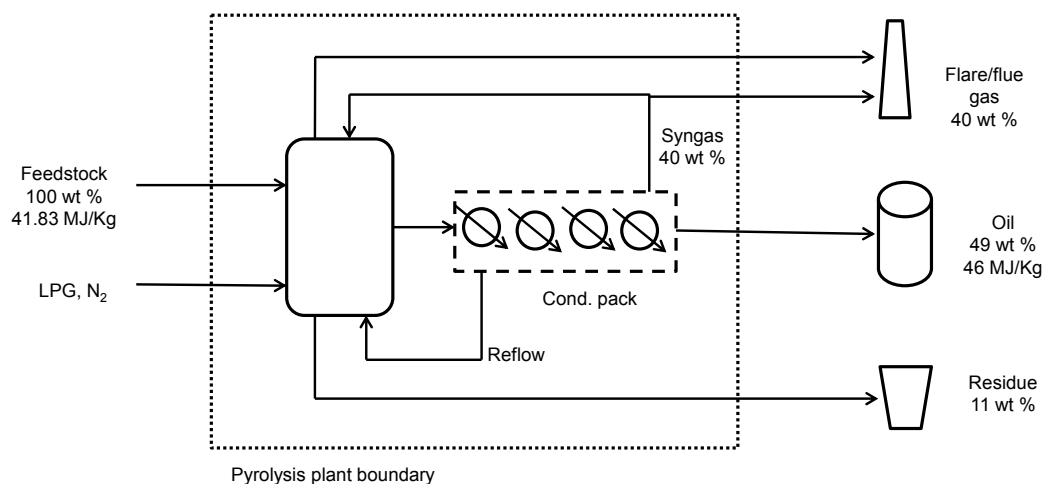
Figure 2. Mass and energy balance of the pyrolysis plant.

2.1.1. Pyrolysis Oil Quality

The total pyrolysis oil produced included a wide boiling-point range of molecules that cover all transportation fuel standards (naphtha, kerosene, diesel, and 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 [9]) and distillation (test method D86 [10]), the total pyrolysis oil can render various transportation fuel products, namely naphtha, diesel, and wax, of different boiling-point ranges. The temperatures that have been used as cut points for the naphtha and diesel fractions are presented in Column 3 (Notes) in Table 1.

Table 1. Pyrolysis oil analysis.

Property	Value	Notes
°API *	46.3	-
Density	796.0 kg/m^3	-
0 recovered (IBP **)	82.0 °C	-
10% recovered	129.5 °C	-
20% recovered	157.0 °C	-
30% recovered	177.5 °C	T 170 at 26.5%
40% recovered	212.5 °C	-
50% recovered	244.5 °C	-
60% recovered	276.0 °C	-
70% recovered	301.5 °C	-
80% recovered	325.5 °C	-
90% recovered	372.5 °C	T 370 at 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

* °API $= \frac{141.5}{SG} - 131.5$ where SG = specific gravity at 60 °F; ** IBP: Initial boiling point; *** EP: End point.

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 %).

2.1.2. Mid-Distillate Fraction Quality

As was aforementioned, the pyrolysis oil can be valorized better if it is 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 diesel fuel. The properties of the mid-distillate fraction are given in Table 2, juxtaposed with the corresponding EN 590 quality specifications [11].

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

Property	Value	Unit	Limits		Test Method
			Min	Max	
Density at 15 °C	802.7	kg/m^3	820.0	845.0	EN ISO 12185 [12]
Viscosity at 40 °C	2.300	mm^2/s	2.000	4.500	EN ISO 3104 [13]
Sulfur Content	42.9	mg/kg	-	10.0	EN ISO 20846 [14]
Aromatic Hydrocarbons	-	wt %	-	-	EN 12916 [15]
Mono	7.7	wt %	-	-	-
Di	1.9	wt %	-	-	-
Tri+	0.4	wt %	-	-	-
Polyaromatic Hydrocarbons	2.3	wt %	-	8	EN 12916 [15]
Distillation	-	-	-	-	EN ISO 3405 [16]
Recovered at 250 °C	36.3	% vol	-	65	-
Recovered at 350 °C	93.8	% vol	85	-	-
95% (*V/V*) Recovered at	354.5	°C	-	360	-
Residue	1.6	% vol	-	-	-
IBP	133.7	°C	-	-	-
10%	204.3	°C	-	-	-
50%	291.3	°C	-	-	-
90%	346.7	°C	-	-	-
95%	354.5	°C	-	-	-
FBP *	368.7	°C	-	-	-
Cetane Number	60.7	-	51	-	EN 15195 [17]
Cetane Index	66.7	-	46	-	EN ISO 4264 [18]
Flash Point	48.0	°C	55	-	EN ISO 2719 [19]
Copper Corrosion (3 h at 50 °C)	1A	-	1A	-	EN ISO 2160 [20]
Cloud Point	-	°C	-	-	EN 3015 [21]
Pour Point	−2	°C	-	-	ISO 3016 [22]
CFPP **	−1	°C	-	-	EN 116 [23]
Lubricity Corrected WSD1.4 at 60 °C	276	μm	-	460	EN ISO 12156-1 [24]
Carbon Residue	0.05	wt %	-	0.3	EN ISO 10370 [25]
Ash Content	<0.005	wt %	-	0.01	EN ISO 6245 [26]
Water Content	51	mg/kg	-	200	EN ISO 12937 [27]
Total Contamination	<12	mg/kg	-	24	EN 12662 [28]
Oxidation Stability	49.0	g/m^3	-	25	EN ISO 12205 [29]
Oxidation Stability	42.43	min	-	-	ASTM D7545 [30]
Manganese content	<0.5	mg/L	-	2	EN 16576 [31]
FAME content ***	<0.1	% vol	-	7.0	EN 14078 [32]
Elemental Analysis	-	-	-	-	-
Carbon Content	85.44	wt %	-	-	ASTM D5291 [33]
Hydrogen Content	14.55	wt %	-	-	ASTM D5291 [33]
Bromine Number	35.7	g Br/100 g	-	-	ISO 3839 [34]
Calorific Value	-	-	-	-	ASTM D240 [35]
Gross	46.67	MJ/kg	-	-	-
Net	43.58	MJ/kg	-	-	-

* FBP: Final boiling point; ** CFPP: Cold filter plugging point; *** FAME: Fatty acid methyl esters.

The mid-distillate fraction of the pyrolysis oil for the most part abides by the EN 590 diesel fuel specifications, which renders it a potential diesel component. According to Table 2, the density of the mid-distillate (802.7 kg/m^3) is slightly lower compared to the EN 590 standards, which range between 820 and 845 kg/m^3. It should be noted that density affects the level of engine power. Furthermore,

kinematic viscosity is another important parameter that affects the performance of diesel fuel pumps and injection systems as it presents the resistance of fuel to flow. The viscosity of the mid-distillate is 2.3 mm^2/s, which meets EN 590 standards. The cetane number (CN) as well as the cetane index (CI) presents the ability for auto-ignition of the fuel; in general, high values of CN and CI improve the engine performance. Mid-distillate not only meets the EN 590 standards for the CN and CI, but both the values of the CN (60.7) and CI (66.7) are significantly higher than the minimum value of EN 590 (CN: 51 and CI: 46), giving an advantage to mid-distillate. As far as the bromine number of the pyrolysis mid-distillate is concerned, it is 35.7 g Br/100 g, which is a very strong indication of olefins' presence in the sample as a product of the pyrolysis process. Finally, lubricity defines the ability of fuel to minimize damage between surfaces in relative motion under load in internal combustion engines. According to Table 2, the lubricity is lower (276 μm) than the maximum limit value of the EN 590 specifications. On the other hand, there are some properties that do not meet the EN 590 standards for diesel fuel. The problematic properties include a higher sulfur content than the minimum of 10 mg/kg, a slightly low flash point, and higher oxidation stability. The Sulfur should have an organic origin, being a leftover of organic anaerobic biodegradation occurring in the landfill for many years, as plastic has virtually no Sulfur. However, another problematic characteristic of the mid-distillate fraction of the pyrolysis oil was its color, which is usually dark brown and not "clear and bright" as is normally expected for diesel fuels. In order to overcome these three diesel specification violations, an additional catalytic hydrotreatment step was considered.

2.2. Pyrolysis Oil Hydrotreatment

Catalytic hydrotreatment is a key refinery process that enables heteroatom removal and saturation reactions, leading to a significant improvement in the quality of the treated fuels [36]. Moreover, catalytic hydrotreatment is foreseen as a key upgrading process for the valorization of bio-based feedstocks, such as lipids [37–39], pyrolysis oils [40,41], and bio-oils [42,43], for the production of high quality renewable fuels. As a result, this process was considered to be the necessary conversion step for the conversion of the mid-distillate fraction of pyrolysis oil to diesel fuel.

The catalytic hydrotreatment of the mid-distillate fraction of pyrolysis oil was conducted in CERTH's hydroprocessing pilot plant (Figure 3). The mass balance of the catalytic hydrotreating of the mid-distillate fraction of the pyrolysis oil is shown in Figure 4, 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.
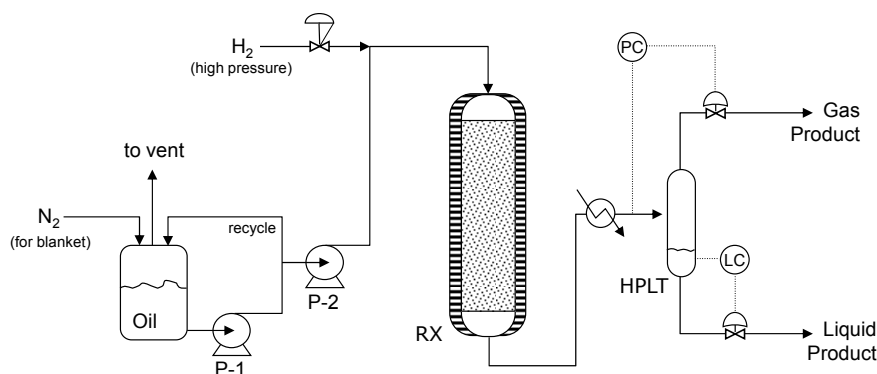

Figure 3. Simplified schematic diagram of the catalytic hydroprocessing pilot plant of the Centre for Research and Technology Hellas (CERTH) employed for the conversion of the pyrolysis oil mid-distillate fraction to diesel. RX: Reactor, HPLT: high pressure low temperature.
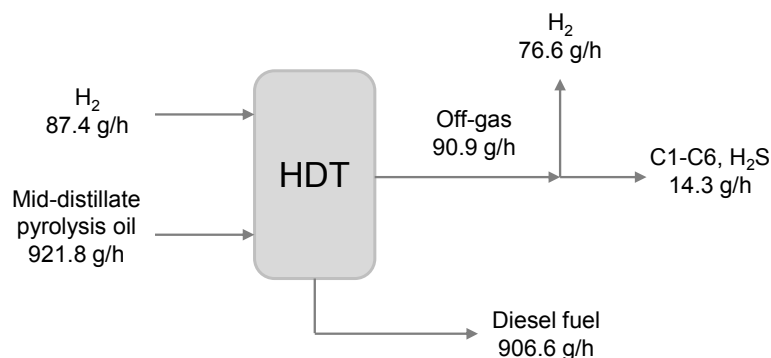
Figure 4. Mass balance of the catalytic hydrotreatment (HDT) of the mid-distillate pyrolysis oil fraction as estimated from the hydrotreating experiments at CERTH.

The diesel fuel produced from upgrading the mid-distillate pyrolysis oil fraction during the experimental testing at CERTH was a clear fuel (Figure 5) with average sulfur of 12.1 mg/kg (see Table 3). 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 5. Mid-distillate fraction of waste plastics pyrolysis oil before (left) and after (right) catalytic hydrotreatment upgrading at CERTH.

2.3. Diesel Fuel Quality

The results of the analysis of the final product are given in Table 3. As seen from the data in Tables 2 and 3, most of the properties that were out of EN 590 specification limits for automotive diesel have been substantially improved. The hydroprocessed fuel has an excellent cetane number that approaches 75. The density and viscosity have been slightly decreased. The polyaromatic hydrocarbons content has been eliminated, and only a very small amount of monoaromatic hydrocarbons is still present in the fuel. All of these characteristics are an indication of a fuel with high paraffinic hydrocarbons content [44]. The values of the cold flow properties are also in accordance with a paraffinic-type fuel.

Regarding the properties of the mid-distillate fraction of the pyrolysis oil that were out of EN 590 standard specifications limits, there was a clear reduction in sulfur content from 43 to 12 mg/kg, but the hydroprocessed fuel still fails to meet the specification of 10 mg/kg. Sulfur in diesel fuel contributes to the formation of particulate matter (PM) in the engine's exhaust and affects the

performance of vehicle emissions control equipment. It has therefore an indirect effect on emissions of CO, hydrocarbons, and NO_X [45]. However, it should be mentioned that the deviation from the specification limit is very small, and it is assumed that with a small modification of the hydroprocessing operating conditions (hydrotreating temperature, pressure, liquid hourly space velocity, and H_2/liquid feed ratio) the fuel will meet the specification limit. In the case of oxidation stability, the hydroprocessed fuel meets the specification limit, and the reduction achieved by the hydroprocessing is very important, as the value was reduced from 49 to 2.1 g/m^3. Oxidation stability is related to the presence of olefins in the fuel, which are more prone to oxidation and the formation of insoluble measured by EN ISO 12205 (similar to ASTM D2274) [46,47]. The method that is used in the petroleum industry for the indirect determination of olefins is the bromine number. The bromine number was determined in both samples, and for the pyrolysis mid-distillate it was measured at 35.7 g/100 g, while for the hydroprocessed sample the relevant value was below 0.1 g/100 g. These values are a strong indication of the presence of olefinic hydrocarbons in the pyrolysis oil, which were eliminated during the hydroprocessing reactions. An FTIR analysis run on both samples showed clear peaks in the area of C=C bonds absorption: strong absorption at 1641 cm^{-1} (C=C stretching of monosubstituted alkenes at 1648–1638 cm^{-1}, strong absorption at 993, 966, 910, and 889 cm^{-1} (C=C bending of monosubstituted alkenes at 995–985 and 915–905 cm^{-1}, C=C bending of trans-disubstituted alkenes at 980–9360 cm^{-1}, and C=C bending of vinylidene at 895–885 cm^{-1}) [48–50]. These peaks do not appear in the hydroprocessed fuel, as was expected, since the olefins have been saturated (converted to paraffins and isoparaffins) in the hydroprocessing step. Furthermore, the flash point has been slightly improved (it increased from 48.0 °C to 52.5 °C), but still remains below the specification limit of 55 °C. This problem can be corrected by choosing a higher cut point temperature between the naphtha and mid-distillate fractions in order to eliminate low boiling-point components that affect the flash point from the mid-distillate.

The only fuel property that has been significantly deteriorated due to the hydroprocessing of the mid-distillate fraction of the pyrolysis oil was the lubricity, where the wear scar diameter (WSD) was increased from 276 to 552 µm, well above the specification limit of 460 µm. Hydroprocessing removes most of the polar compounds (mainly nitrogen, sulfur, and oxygen compounds) that are present in the fuel, which are responsible for the good lubricity of non-hydroprocessed fuels [51]. This is a common problem for all ultra-low sulfur middle-distillates. The use of fuels with poor lubricity can increase fuel pump and injector wear, and at the extreme cause catastrophic failure; on the other hand, a high-lubricity fuel may provide reduced wear and a longer component life [52].

Table 3. Analysis of the hydroprocessed mid-distillate fraction of the pyrolysis oil.

Property	Value	Unit	Limits		Test Method
			Min	Max	
Density at 15 °C	790.6	kg/m^3	820.0	845.0	EN ISO 12185 [12]
Viscosity at 40 °C	2.377	mm^2/s	2.000	4.500	EN ISO 3104 [13]
Sulfur Content	12.1	mg/kg	-	10.0	EN ISO 20846 [14]
Aromatic Hydrocarbons	-	wt %	-	-	EN 12916 [15]
Mono	1.8	wt %	-	-	-
Di	-	wt %	-	-	-
Tri+	-	wt %	-	-	-
Polyaromatic Hydrocarbons	-	wt %	-	8	EN 12916 [15]
Distillation	-	-	-	-	EN ISO 3405 [16]
Recovered at 250 °C	41.0	vol %	-	65	-
Recovered at 350 °C	95.2	% vol	85	-	-
95% (*V*/*V*) Recovered at	349.5	°C	-	360	-
Residue	1.4	vol %	-	-	-
IBP	146.6	°C	-	-	-
10%	194.7	°C	-	-	-
50%	263.6	°C	-	-	-
90%	331.7	°C	-	-	-
95%	349.5	°C	-	-	-
FBP	360.7	°C	-	-	-

Table 3. *Cont.*

Property	Value	Unit	Limits		Test Method
			Min	**Max**	
Derived Cetane Number	74.7	-	51	-	EN 16144 [53]
Cetane Index	71.5	-	46	-	EN ISO 4264 [18]
Flash Point	52.5	°C	55	-	EN ISO 2719 [19]
Copper Corrosion (3 h at 50 °C)	1A	-	1A	-	EN ISO 2160 [20]
Cloud Point	8	°C	-	-	EN 23015 [21]
Pour Point	2	°C	-	-	ISO 3016 [22]
CFPP	2	°C	-	-	EN 116 [23]
Lubricity Corrected WSD1.4 at 60 °C	552	μm	-	460	EN ISO 12156-1 [24]
Carbon Residue	0.01	wt %	-	0.3	EN ISO 10370 [25]
Ash Content	-	wt %	-	0.01	EN ISO 6245 [26]
Water Content	40	mg/kg	-	200	EN ISO 12937 [27]
Total Contamination	1.2	mg/kg	-	24	EN 12662 [28]
Oxidation Stability	2.1	g/m^3	-	25	EN ISO 12205 [29]
Oxidation Stability	148	min	-	-	ASTM D7545 [30]
Manganese content	-	mg/L	-	2	EN 16576 [31]
FAME content	-	% vol	-	7.0	EN 14078 [32]
Elemental Analysis	-	-	-	-	
Carbon Content	85.14	wt %	-	-	ASTM D5291 [33]
Hydrogen Content	14.85	wt %	-	-	ASTM D5291 [33]
Bromine Number	<0.1	g Br/100 g	-	-	ISO 3839 [34]
Calorific Value	-	-	-	-	ASTM D240 [35]
Gross	46.98	MJ/kg	-	-	-
Net	43.83	MJ/kg	-	-	-

3. Conclusions

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 the EN 590 standard for automotive diesel, and can be considered a promising alternative diesel pool component. The successful conversion of 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's properties are superior to those of biomass pyrolysis oil (bio-oil), which is characterized by high water content and is highly acidic [53,54], and those of scrap tire pyrolysis oil (STPO), which has high sulfur, nitrogen, and metals (Na, Ca, Ti, Fe, Cu, Al, Zn, Pb, and Cr) content [40,55]. If compared to the plastic pyrolysis oil produced by another large-scale plant, whose content of naphtha, diesel, and wax is approximately 25 wt %, 60 wt %, and 15 wt % respectively, with a density of 854.5 kg/m^3 [55], a larger amount of mid-distillate and a smaller amount of wax in the assessed pyrolysis oil is confirmed. As a result, a waste pyrolysis oil upgrade requires a single hydroprocessing step, while the other types of pyrolysis oil require multiple hydroprocessing steps, rendering the upgrading cost unattractive as it constitutes 70–85% of the overall production cost [56].

4. Materials and Methods

4.1. Plastic Waste Pyrolysis Plant

The plastic waste pyrolysis was produced via assessment tests of a pyrolysis plant of plastic waste sorted by an old landfill operating in South East Asia in 2015. The precise composition of the feedstock was unknown, but was estimated to be a majority mixture of PE, PP, and PET, with minor contributions of Polystyrene PS, being entirely packaging materials (bags, liquid containers, bottles, etc.) Unlike most pyrolysis plants operating in batch mode, this plant has semi-continuous operation with a capacity of 5 t/d. The loading of the plastic waste was continuously performed via a modified extruder, and after ~48 h the residues and ash were extracted

without cooling via a water-jacked screw (<5 h duration). Residues extraction was performed after a period when the plant was cooked off, i.e., the reactor is maintained at a hot temperature without loading new feedstock. Then, the waste plastic loading started again and the aforementioned process was repeated. The pyrolysis plant reactor is heated partially via non-condensable gas and partially by LPG (Liquefied Petroleum Gas). The pyrolysis plant's layout has some similarity to the Mikasa and Niigata liquefaction plants in Japan [57], but without any plastic pre-treatment and with an enhanced feeding device capable of keeping the reactor sealed. The plant employs fractional condensation to separate heavy hydrocarbons, which is pumped back into the pyrolysis reactor, from the main oil stream, while a portion of light condensate is directly used on site as a gasoline substitute for power generators. Figure 1 shows the simplified process scheme. The proper sizing of the pyrolysis reactor and the oil condensers was a key prerequisite for the commercial operation and functionality of the plant. A 3 L sample of the mid-distillate fraction was obtained from the distillation of approximately 30 L of raw pyrolysis oil obtained during normal operation of the pyrolysis plant.

4.2. Catalytic Hydrotreatment Plant

For the experimental testing, the hydroprocessing pilot plant VB01 of CERTH was employed, which is schematically depicted in Figure 3. The VB01 hydroprocessing plant operates in continuous mode 24/7 at typical operating regimes of industrial hydroprocessing units (i.e., maximum system pressure 150 barg, maximum reactor temperature 450 °C, H_2/oil up to 10,000 scfb). The VB01 hydroprocessing plant consists of (a) the feed system, (b) the reactor system, and (c) the product separation and collection system. The feedstock is loaded into the feed system, consisting of a heated feed-tank with recycling, which allows for both the controlled heating and homogeneity of the feedstock. The feedstock is compressed and then mixed with high pressure H_2, entering the reactor system which consists of six independent heated zones allowing for isothermal operation. The reactor effluent finally enters a high-pressure low-temperature separator, which allows for liquid and gas product retrieval.

For the experimental testing of the potential of upgrading pyrolysis oil via a catalytic hydrotreatment, 3 L of the mid-distillate fraction of the pyrolysis oil were sent to CERTH. The mid-distillate fraction of the pyrolysis oil was a dark brown colored sample (Figure 5), visually resembling heavy oil, which was loaded in the VB01 catalytic hydroprocessing pilot plant of CERTH (Figure 3) without any pretreatment. The hydroprocessing testing employed a commercial $NiMo/Al_2O_3$ hydrotreating catalyst and typical hydrotreating conditions (system pressure 80–100 barg, reactor temperature 350–375 °C, H_2/oil ratio 5000 scfb, liquid hourly space velocity 1 h^{-1}).

4.3. Final Product Quality

In order to evaluate the potential for utilizing the upgraded mid-distillate fraction of the pyrolysis oil as a drop-in diesel fuel, a 1 L sample was sent to the Fuels and Lubricants Technology Laboratory of the National Technical University of Athens (Greece). The analysis of the sample was made by employing mainly the test methods described in the EN 590 standard for automotive diesel fuel.

References and Notes

1. Wong, S.L.; Ngadi, N.; Abdullah, T.A.T.; Inuw, I.M. Current state and future prospects of plastic waste as source of fuel: A review. *Renew. Sustain. Energy Rev.* **2015**, *50*, 1167–1180. [CrossRef]
2. Kalargaris, I.; Tian, G.; Gu, S. The utilisation of oils produced from plastic waste at different pyrolysis temperatures in a DI diesel engine. *Energy* **2017**, *131*, 179–185. [CrossRef]

3. Hoornweg, D.; Bhada-Tata, P. What a Waste—A Global Review of Solid Waste Management. World Bank Urban Development Series Knowledge Papers 2012. Available online: www.worldbank.org/urban (accessed on 12 June 2017).

4. United Nations Environmental Program. Converting Waste Plastic into a Resource. 2009. Available online: http://www.unep.or.jp/ (accessed on 12 June 2017).

5. Sharuddin, S.D.A.S.; Abnisa, F.; Daud, W.M.A.W.; Aroua, M.K. Energy recovery from pyrolysis of plastic waste: Study on non-recycled plastics (NRP) data as the real measure of plastic waste. *Energy Convers. Manag.* **2017**, *148*, 925–934. [CrossRef]

6. Murugan, S.; Ramaswamy, M.C.; Nagarajan, G. Assessment of pyrolysis oil as an energy source for diesel engines. *Fuel Process. Technol.* **2009**, *90*, 67–74. [CrossRef]

7. Ratnasari, D.K.; Nahil, M.A.; Williams, P.T. Catalytic pyrolysis of waste plastics using staged catalysis for production of gasoline range hydrocarbon oils. *J. Anal. Appl. Pyrolysis* **2017**, *124*, 631–637. [CrossRef]

8. Kaimal, V.K.; Vijayabalan, P. A study on synthesis of energy fuel from waste plastic and assessment of its potential as an alternative fuel for diesel engines. *Waste Manag.* **2016**, *51*, 91–96. [CrossRef] [PubMed]

9. *ASTM D86-16a Standard Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure*; ASTM International: West Conshohocken, PA, USA, 2016.

10. *ASTM D4052-16 Standard Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter*; ASTM International: West Conshohocken, PA, USA, 2016.

11. *Automotive Fuels-Diesel-Requirements and Test Methods*; EN 590:2013; European Committee for Standardization (CEN): Brussel, België, 2013.

12. Crude Petroleum and Petroleum Products—Determination of Density—Oscillating U-Tube Method. International Organization for Standardization ISO 12185:1996. Available online: https://www.iso.org/standard/21124.html (accessed on 31 October 2017).

13. Petroleum Products—Transparent and Opaque Liquids—Determination of Kinematic Viscosity and Calculation of Dynamic Viscosity. ISO 3104:1994. International Organization for Standardization. Available online: https://www.iso.org/standard/8252.html (accessed on 31 October 2017).

14. Petroleum Products—Determination of Sulfur Content of Automotive Fuels—Ultraviolet Fluorescence Method. ISO 20846:2011. International Organization for Standardization. Available online: https://www.iso.org/standard/51774.html (accessed on 31 October 2017).

15. Petroleum Products—Determination of Aromatic Hydrocarbon Types in Middle Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection. European Committee for Standardization (CEN) EN 12916:2016. Available online: https://www.sis.se/api/document/preview/8018972/ (accessed on 31 October 2017).

16. Petroleum Products—Determination of Distillation Characteristics at Atmospheric Pressure. International Organization for Standardization ISO 3405:2011. Available online: https://www.iso.org/standard/44095.html (accessed on 31 October 2017).

17. Liquid Petroleum Products—Determination of Ignition Delay and Derived Cetane Number (DCN) of Middle Distillate Fuels by Combustion in a Constant Volume Chamber. EN 15195:2014. European Committee for Standardization (CEN). Available online: https://infostore.saiglobal.com/preview/is/en/2014/i.s.en15195-2014.pdf?sku=1774892 (accessed on 31 October 2017).

18. Petroleum Products—Calculation of Cetane Index of Middle-Distillate Fuels by the Four-Variable Equation. ISO 4264:2007. International Organization for Standardization. Available online: https://www.iso.org/standard/45627.html (accessed on 31 October 2017).

19. Determination of Flash Point—Pensky-Martens Closed Cup Method. ISO 2719:2016. International Organization for Standardization. Available online: https://www.iso.org/standard/62263.html (accessed on 31 October 2017).

20. Petroleum Products—Corrosiveness to Copper—Copper Strip Test. ISO 2160:1998. International Organization for Standardization. Available online: https://www.iso.org/standard/27552.html (accessed on 31 October 2017).

21. Petroleum Products—Determination of Cloud Point. ISO 3015:1992. International Organization for Standardization. Available online: https://www.iso.org/standard/8095.html (accessed on 31 October 2017).

22. Petroleum Products—Determination of Pour Point. ISO 3016:1994. International Organization for Standardization. Available online: https://www.iso.org/standard/20721.html (accessed on 31 October 2017).

23. CEN. Diesel and Domestic Heating Fuels—Determination of Cold Filter Plugging Point—Stepwise Cooling Bath Method; EN 116:2015; European Committee for Standardization, 2015.

24. Diesel Fuel—Assessment of Lubricity Using the High-Frequency Reciprocating Rig (HFRR)—Part 1: Test Method. ISO 12156-1:2016. International Organization for Standardization. Available online: https://www.iso.org/standard/65227.html (accessed on 31 October 2017).

25. Petroleum Products—Determination of Carbon Residue—Micro Method. ISO 10370:2014. International Organization for Standardization. Available online: https://www.iso.org/standard/57081.html (accessed on 31 October 2017).

26. Petroleum Products—Determination of Ash. ISO 6245:2001. International Organization for Standardization. Available online: https://www.iso.org/standard/31156.html (accessed on 31 October 2017).

27. Petroleum Products—Determination of Water—Coulometric Karl Fischer Titration Method. ISO 12937:2000. International Organization for Standardization. Available online: https://www.iso.org/standard/2730.html (accessed on 31 October 2017).

28. CEN. Liquid Petroleum Products—Determination of Total Contamination in Middle Distillates, Diesel Fuels and Fatty Acid Methyl Esters; EN 12662:2014; European Committee for Standardization, 2014.

29. Petroleum Products—Determination of the Oxidation Stability of Middle-Distillate Fuels. ISO 12205:1995. International Organization for Standardization. Available online: https://www.iso.org/standard/21187.html (accessed on 31 October 2017).

30. *ASTM D7545-14 Standard Test Method for Oxidation Stability of Middle Distillate Fuels—Rapid Small Scale Oxidation Test (RSSOT)*; ASTM International: West Conshohocken, PA, USA, 2016.

31. CEN. Automotive Fuels—Determination of Manganese and Iron Content in Diesel—Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) Method; EN 16576:2014; European Committee for Standardization, 2014.

32. CEN. Liquid Petroleum Products—Determination of Fatty Acid Methyl Ester (FAME) Content in Middle Distillates—Infrared Spectrometry Method; EN 14078:2014; European Committee for Standardization, 2014.

33. *ASTM D5291-16 Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants*; ASTM International: West Conshohocken, PA, USA, 2016.

34. *Petroleum Products—Determination of Bromine Number of Distillates and Aliphatic Olefins—Electrometric Method*; ISO 3839:1996. International Organization for Standardization. Available online: https://www.iso.org/standard/22154.html (accessed on 31 October 2017).

35. *ASTM D240-17 Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter*; ASTM International: West Conshohocken, PA, USA, 2016.

36. Bezergianni, S.; Kalogianni, A.; Dimitriadis, A. Catalyst evaluation for waste cooking oil hydroprocessing. *Fuel* **2012**, *93*, 638–641. [CrossRef]

37. Bezergianni, S.; Dimitriadis, A.; Chrysikou, L. Quality and Sustainability Comparison of One- vs. Two-step Catalytic Hydroprocessing of Waste Cooking Oil. *Fuel* **2014**, *118*, 300–307. [CrossRef]

38. Bezergianni, S.; Dimitriadis, A.; Kalogianni, A.; Knudsen, K.G. Toward Hydrotreating of Waste Cooking Oil for Biodiesel Production. Effect of Pressure, H_2/Oil Ratio, and Liquid Hourly Space Velocity. *Ind. Eng. Chem. Res.* **2011**, *50*, 3874–3879. [CrossRef]

39. Gomes, J.R.; Bezergianni, S.; Luiz Zotin, J.; Falabella Sousa-Aguiar, F. Biofuels Generation via Hydroconversion of Vegetable Oils and Animal Fats. In *Catalytic Hydrogenation for Biomass Valorization*; RSC Environmental Series; Royal Society of Chemitry: Cambridge, UK, 2014; Chapter 9; pp. 204–222. ISBN 978-1-84973-801-9.

40. Hita, I.; Gutiérrez, A.; Olazar, M.; Bilbao, J.; Arandes, J.S.; Castaño, P. Upgrading model compounds and Scrap Tires Pyrolysis Oil (STPO) on hydrotreating NiMo catalysts with tailored supports. *Fuel* **2015**, *145*, 158–169. [CrossRef]

41. Dimitriadis, A.; Bezergianni, S. Biomass vs. Plastic Pyrolysis Oil Upgrading via Hydrotreating. In Proceedings of the II Scientific-Technological Symposium Catalytic Hydroprocessing in Oil Refining, Belgrade, Serbia, 17–23 April 2016.

42. Yang, Z.; Kumar, A.; Huhnke, R.L. Review of Recent Developments to Improve Storage and Transportation Stability of Bio-oil. *Renew. Sustain. Energy Rev.* **2015**, *50*, 859–870. [CrossRef]

43. Elliott, D.C. Biofuel from Fast Pyrolysis and Catalytic Hydrodeoxygenation. *Curr. Opin. Chem. Eng.* **2015**, *9*, 59–65. [CrossRef]

44. Karonis, D.; Chilari, D.; Manou, C. Characterization of Hydroprocessed Used Cooking Oils in Blend with Low Quality Gasoil Samples. *SAE Int. J. Fuels Lubr.* **2014**, *7*, 250–262. [CrossRef]

45. Bezergianni, S.; Dimitriadi, A. Comparison between different types of renewable diesel. *Renew. Sustain. Energy Rev.* **2013**, *21*, 110–116. [CrossRef]

46. Kalitchin, Z.D.; Ivanov, S.K.; Tanielyan, S.K.; Boneva, M.I.; Georgiev, P.T.; Ivanov, A.; Kanariev, K. Chemical stability of diesel fuels and sediment formation therein: 1. Evaluation of the chemical stability of diesel fuels by following the kinetics of sediment. *Fuel* **1992**, *71*, 437–442. [CrossRef]

47. Owczuk, M.; Kołodziejczyk, K. Liquid Fuel Ageing Processes in Long-term Storage. In *Storage Stability of Fuels*; Biernat, K., Ed.; InTech: Rijeka, Croatia, 2015; pp. 101–129. ISBN 978-953-51-1734-6. [CrossRef]

48. Pretsch, E.; Bühlmann, P.; Badertscher, M. *Structure Determination of Organic Compounds*; Springer: Berlin, Germany, 2009; pp. 272–275. ISBN 978-3-540-93809-5.

49. Coates, J. Interpretation of Infrared Spectra, a Practical Approach. In *Encyclopedia of Analytical Chemistry*; Meyers, R.A., Ed.; John Wiley & Sons Ltd.: Hoboken, NJ, USA, 2000; pp. 10815–10837.

50. Silverstein, R.M.; Webster, F.X.; Kiemle, D.J. *Spectrometric Identification of Organic Compounds*, 7th ed.; John Wiley & Sons Ltd.: Hoboken, NJ, USA, 2005; pp. 85–86. ISBN 0-471-39362-2.

51. Bruno, T.J.; Hsieh, P.Y. A perspective on the origin of lubricity in petroleum distillate motor fuels. *Fuel Process. Technol.* **2015**, *129*, 52–60. [CrossRef]

52. Bacha, J.; Freel, J.; Gibbs, A.; Hemighaus, G.; Hoekman, K.; Horn, J.; Ingham, M.; Jossens, L.; Kohler, D.; Lesnini, D.; et al. *Diesel Fuels Technical Review*; Chevron: San Ramo, CA, USA, 2007.

53. Zhang, Z.; Pittman, C.U.; Sui, S.; Sun, J.; Wang, Q. Catalytic Upgrading of Bio-Oil by Reacting with Olefins and Alcohols over Solid Acids: Reaction Paths via Model Compound Studies. *Energies* **2013**, *6*, 1568–1589. [CrossRef]

54. Oasmaa, A.; Peacocke, C.; Gust, S.; Meier, D.; McLellan, R. Norms and Standards for Pyrolysis Liquids. End-User Requirements and Specifications. *Energy Fuels* **2005**, *19*, 2155–2163. [CrossRef]

55. Pilusa, T.J.; Shukla, M.; Muzenda, E. Pyrolitic Tyre Derived Fuel: A Review. In Proceedings of the International Conference on Chemical, Mining and Metallurgical Engineering (CMME'2013), Johannesburg, South Africa, 27–28 November 2013.

56. Oasmaa, A.; Kuoppala, E.; Ardiyanti, A.; Venderbosch, R.H.; Heeres, H.J. Characterization of Hydrotreated Fast Pyrolysis Liquids. *Energy Fuels* **2010**, *24*, 5264–5272. [CrossRef]

57. Okuwaki, A.; Yoshioka, T. The liquefaction of plastic containers and packaging in Japan. In *Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels*; Wiley: Edithvale, Australia, 2006; pp. 663–708.