Article
Comparison of Antioxidants to Increase the Oxidation Stability of Pyrolysis Oils of Three Plastics Using Iodine Value

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Abstract: Pyrolysis is an excellent method for recovering mixed and contaminated plastics that are no longer recyclable. Special attention must be paid to the stability of the fuel to avoid the formation of undesirable products. This can be achieved by additives such as antioxidants. In this study, high-density polyethylene, polypropylene, and polystyrene plastic waste are slowly pyrolyzed to a maximum of 470 degrees Celsius. A gasoline fraction (0–190 °C) and a diesel fraction (190–320 °C) are then obtained from these. Three antioxidants are added to these fractions: pyrocatechol, phenol, and freshly produced algal pyrolysis oil; the latter is described in the literature as containing particularly high levels of antioxidants. The oxidation stability of these mixtures and the change in the iodine number over time are measured using a newer method than the commonly used method of Wijs. Phenol improves the oxidation stability best, followed successively by algae pyrolysis oil and pyrocatechol. The oxidation stability of the gasoline fraction of the polypropylene pyrolysis oil with phenol is 49% higher than that of the same fraction without antioxidants.

Keywords: pyrolysis; high-density polyethylene; polypropylene; polystyrene; iodine value; oxidation stability; antioxidants; phenol; pyrocatechol

1. Introduction

Plastics and their products are an integral part of modern life. The production of plastics has increased significantly since 1950, reaching 348 million tons in 2017 [1]. The increasing production of polymers is due to the rapid increase in the world population, which is accompanied by economic growth and better living conditions [2,3]. In addition, the increasing popularity of plastics is due to their properties, such as lightness, durability, low cost, and wide applicability. It is estimated that about 33% of all plastics produced annually are single-use plastics and typically end up in landfills within 12 months of production, and 15–40% of used plastics end up in the oceans [4].

In general, there are three main methods for plastic waste management: mechanical and chemical recycling, incineration, and landfilling [5]. In 2016, for the first time in Europe, the amount of plastic waste recycled (31.1%) was higher than the amount landfilled (27.3%). However, the majority of plastics (41.6%) were incinerated [6].

According to European law, landfilling of plastic waste should be the last resort, when no other alternatives are available [7]. The European strategy for the transition to a circular economy makes measures to reduce plastic waste and promote its reuse a priority.

Currently, one of the most attractive and popular recycling options for plastic waste is pyrolysis, in which the polymer chains of plastics are broken down into molecules of lower molecular weight by breaking the C-C and C-H bonds in an oxygen-free or oxygen-deficient environment at elevated temperatures [8].

Pyrolysis is an excellent method for recovering mixed and contaminated plastics that are no longer recyclable [9,10]. This thermal process has been successfully used to convert...
all types of plastic waste into liquid pyrolysis oil. In addition, pyrolysis is probably the only way to fully recover plastic waste that can be converted into more valuable petroleum products instead of being permanently landfilled [11].

The main product of the plastic pyrolysis process, pyrolysis oil, has similar physicochemical properties to fuels. Crude pyrolysis oil is generally a hydrocarbon mixture consisting of compounds with C₅-C₂₅ carbon atoms, with a dynamic viscosity between 1.77 and 1.90 mPa s, a kinetic viscosity in the range of 1.92 to 2.09 cSt, a pour point in the range of 11 °C to −60 °C, a density between 0.71 and 0.92 g/cm³, and a flash point between 28.1 °C and 30.2 °C. Due to their high calorific value (>40 MJ/Kg), plastic oils are of particular interest for the production of alternative fuels [12]. Pyrolysis oils need to be treated and modified to achieve the properties of standardized fuels. Modification processes aim to stabilize the crude pyrolysis oil, reduce aging potential, and remove particulates so that the oil or its blends can be used in diesel engines. Pyrolysis oils can be treated by physical and chemical methods [13,14].

Various additives, such as oxygenates, antioxidants, combustion promoters, anti-knock agents, etc., are added to fuels (including alternative fuels) to improve their properties, reduce emissions, and increase engine performance. Special attention is paid to fuel stability. Fuel stability is the resistance of the fuel to degradation processes that can change the properties of the fuel by forming undesirable products [15,16].

Phenolic antioxidants are widely used in the fuel industry to stabilize fuels due to their cost, availability, and effectiveness. According to their origin, antioxidants can be classified as synthetic and natural [17,18]. The best-known phenolic antioxidants are as follows: (a) dibutylhydroxytoluene (BHT), (b) butylhydroxyanisole (BHA), (c) tert-butylhydroquinone (TBHQ), (d) propyl gallate (PG), and (e) pyrogallol (PY) [19]. In most cases, it is found that the effectiveness of phenolic antioxidants with an increase in the content of antioxidants up to 1000 ppm also increases the oxidation stability of the fuel. Another source of antioxidants is algae pyrolysis oil, which, according to the literature [20], is rich in them. Antioxidants from an algae pyrolysis oil have the advantage that algae can be used as a renewable source instead of synthetic antioxidants obtained from fossil raw materials.

In this study, a method for evaluating the potential of pyrolysis oils from plastic waste for the production of alternative fuels is presented. High-density polyethylene (HDPE), polypropylene (PP), and polystyrene (PS) plastic wastes were slowly pyrolyzed to a maximum temperature of 470 degrees Celsius. Then, distilled at atmospheric pressure, the oils were separated into a gasoline fraction (0–190 °C) and a diesel fraction (190–320 °C). Three antioxidants were added to these distillates: pyrocatechol, phenol, and freshly prepared algae pyrolysis oil from another study. The oxidation stability and the change in the iodine number over time according to the method described in the literature [21–24] were determined and discussed.

2. Materials and Methods

2.1. Materials

The raw materials used for pyrolysis were high-density polyethylene (HDPE), polypropylene (PP), and polystyrene (PS), which came from a secondary sorting plant (JSC Waste Management Center of Klaipeda Region, Klaipeda, Lithuania). Algae pyrolysis oil comes from another study, whose results were published in [21]. In this study, macroalgae of the species Cladophora glomerata from the northern beach of Klaipeda (Lithuania) were heated to three different final pyrolysis temperatures. The greatest carbon conversion was obtained with a pyrolysis oil that was heated to a final pyrolysis temperature of 350 °C. The properties of this pyrolysis oil of macroalgae are listed in the following Table 1 and was used in this study.

Acetic acid (100%), sodium carbonate (≥99.5%), iron(II) sulfate (97%), potassium permanganate (≥99.0%), potassium iodide (puriss.), iodine (≥99.8%), ethanol (96%), sodium thiosulfate pentahydrate Na₂S₂O₃·5H₂O (≥99.5%), potato starch (ign. residue ≤ 0.5%),
phenol (99.0–100%), and pyrocatechol (1,2-dihydroxybenzene) (≥99%) were purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany).

Table 1. Properties of pyrolysis oil of macroalgae from [21].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg m$^{-3}$)</td>
<td>992 ± 1</td>
</tr>
<tr>
<td>Viscosity (mm$^2$ s$^{-1}$)</td>
<td>0.984 ± 0.001</td>
</tr>
<tr>
<td>Calorific value (MJ kg$^{-1}$)</td>
<td>23.5 ± 0.6</td>
</tr>
<tr>
<td>Water content (%)</td>
<td>18 ± 0.5</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>6.1386 ± 0.2688</td>
</tr>
</tbody>
</table>

2.2. Procedure of the Pyrolysis

Pyrolysis was carried out at atmospheric pressure in a non-stirred 4.5 L steel batch reactor (internal height 295 mm, internal diameter 190 mm) with a single outlet. The thermocouple in a sleeve protrudes 140 mm from the top into the reactor chamber. The reactor stands upright in the muffle furnace, with the reactor head (60 mm internal height) protruding from the furnace. The outlet from the top plate on the reactor head opens via an air-cooled connection into a double-neck adapter, which sits in a flask for the pyrolysis oil and is connected to a water-cooled reflux condenser (about 15 °C temperature) on the 2nd neck. The reflux condenser is only used for complete condensation of the pyrolysis oil. The furnace heats the bottom and the side wall of the reactor to the desired temperature. The pyrolysis system is shown in Figure 1.

![Figure 1. Slow pyrolysis system: 1—electric muffle furnace, 2—reactor, 3—pressure sensor, 4—thermocouple, 5—valve-pressure regulator, 6—air cooler-condenser, 7—liquid product collection container, 8—water cooler-condenser, 9—safety valves, 10—pressure sensor, 11—gas product volume measurement counter, 12—gas burner.](image-url)

The reactor was charged with 500 g of each polymer by pressing in. After closing and connecting the reactor, it was placed in the furnace and connected to the connecting piece to the flask and reflux cooler. The heating rate was 2–3 °C min$^{-1}$, with an average residence time of about 2 h, with the temperature in the reactor rising after about 15 min after switching on. When the furnace is switched on and the final temperature has been
reached, it is maintained at this temperature until no further drop of condensate flows into the flasks within a time interval of 10 min. The condensed liquid product (pyrolysis oil) was collected in a receiving flask made of glass; the gas was released into the atmosphere through the tube installed in the reactor; the solid residue remained in the reactor and was removed from it at the end of the process. The liquid phase was filtered through Whatman No. 4 filter paper to remove solids and placed in a refrigerator until further analysis. The pyrolysis was realized in three replicates.

The mass balance was determined as the difference between the weight of the sample and the sum of the liquid, and the solid was equal to the amount of gas.

2.3. Distillation of the Pyrolysis Oil to Obtain the Hydrocarbon Fraction for Gasoline and Diesel

The test was performed according to ASTM D 86-96. For this purpose, the distillation was carried out using the EIE-149DNRS petroleum distillation apparatus (EIE Instruments, India). The distillation unit consists of a distillation flask with a branch in the neck, into which a thermocouple is inserted (for temperature monitoring), a heating element (maximum temperature 600 °C), a water-cooling bath, and a measuring cylinder for collecting and measuring the volume of the condensate. In our experiment, 100 mL of the pyrolysis oil is added to the distillation flask, and then a thermocouple is inserted into the flask. The distillation flask is placed on the heating element, and the heater is turned on. After the pyrolysis oil begins to evaporate, the steam enters the water-cooling bath via the piston branch and is condensed. With liquid products, condensed vapors enter the measuring cylinder. First, the gasoline fraction is collected up to a temperature of 190 °C, and then the diesel fraction (from 190 °C) to 320 °C is collected in another measuring cylinder. The residue fraction with a boiling point > 320 °C results from the difference in the volumes of the sum of the gasoline and diesel fractions to the original volume of the pyrolysis oil.

2.4. Production of the Mixtures

Mixtures are prepared from distillates of pyrolysis oils and antioxidants (phenol, pyrocatechol) or algae pyrolysis oil. To prepare mixtures with antioxidants, add 0.5% (by weight of distillate) of the antioxidant to 10–15 mL of the gasoline or diesel fraction and stir with a magnetic stirrer for 5 min or until the substance is completely dissolved. For mixtures with algae oil, add 5% algae oil to 50–60 mL of the gasoline or diesel fraction and stir at 5000 rpm for 30 min with a mechanical stirrer.

2.5. Physical Properties of the Pyrolysis Liquids

The density was determined according to EN ISO 12185 with a DMA 4500 densimeter (Anton Paar GmbH, Graz, Austria). The viscosity was determined according to EN ISO 3104 with a capillary viscometer at 40 °C. The calorific value was determined according to DIN 51900:2000 with an IKA calorimeter CS00300C (IKA-Werke GmbH & Co. KG, Breisgau, Germany). The oxidation stability was determined according to EN 16091 with an automatic oxidation stability analyzer PetroOXY (Anton Paar GmbH). Flash point was determined according to EN 22719 using a Pac FP93 5G2 automatic analyzer (PAC L.P., Houston, TX, USA), which allows for the determination of the flash point of the closed Pensky–Martens crucible of petroleum products. The pour point was determined according to ISO 3016 using a fully automatic CPP 5Gs instrument (PAC L.P.) to measure the pour point of the fuel. The analyses were performed in three replicates.

2.6. Determination of the Iodine Value

The test was performed according to the methodology described in [23,24]. Place 0.1 to 0.15 g of the diesel or gasoline fraction in an Erlenmeyer flask and dissolve in 15 mL of chloroform. Stir the mixture with a magnetic stirrer at 300 rpm for 5 min. Then, stop stirring and add 20 mL of a 0.1 mol/L iodine–potassium iodide solution, and continue stirring. After another 5 min, 200 mL of cold distilled water (about 5 °C) is added to the mixture and stirred again. The conical flask is closed during the entire mixing process
to prevent iodine vapor from escaping into the environment. Then, 3 mL of a 1% starch solution is added to the sample. The sample thus prepared is then titrated with 0.1 mol/L Na$_2$S$_2$O$_3$ solution in the presence of 3.0 mL of the starch solution until the solution has a pale-yellow color. The titration continues until the blue color disappears and a milky solution is formed.

Two samples are titrated for each test product. The third titration is performed with a blank sample without the test product. The iodine number is calculated according to Formula (1):

$$\text{Iodine number} = \frac{(B - A) \times C \times 12.69}{m}$$  \hspace{1cm} (1)

where B is the volume of Na$_2$S$_2$O$_3$ solution used in the titration of the blank sample, mL; A is the volume of Na$_2$S$_2$O$_3$ solution used to titrate the sample with the test product, mL; C is the concentration of the Na$_2$S$_2$O$_3$ solution, mol/L; and m is the mass of the sample weighed for titration, g.

3. Results

3.1. Pyrolysis of the Plastic

The yields of liquid, solid, and gaseous products of the performed pyrolys of HDPE, PP, and PS are shown in Table 2.

<table>
<thead>
<tr>
<th>No.</th>
<th>Type of Plastic</th>
<th>Oil Yield, %</th>
<th>Solid Residue Yield, %</th>
<th>Gas Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>HDPE</td>
<td>90.0 ± 0.72</td>
<td>0.2 ± 0.02</td>
<td>9.8 ± 0.72</td>
</tr>
<tr>
<td>2.</td>
<td>PP</td>
<td>88.6 ± 1.41</td>
<td>0.6 ± 0.15</td>
<td>10.8 ± 1.40</td>
</tr>
<tr>
<td>3.</td>
<td>PS</td>
<td>81.6 ± 1.14</td>
<td>10.0 ± 0.48</td>
<td>8.5 ± 0.66</td>
</tr>
</tbody>
</table>

The oil yields from the pyrolysis of these plastics are in conformity with those reported in the literature [25–27].

3.2. Investigation of the Properties of the Pyrolysis Oils

Parameters such as viscosity and density were determined for pyrolysis oils of various plastics, allowing initial assumptions to be made about the suitability of the oils as feedstocks for fuel production. In addition, the pour point of the oils was determined, which allows for an assessment of the flowability of the oils at low temperatures, and the iodine value, which indicates how many grams of iodine are bound per 100 g of sample and allows for an assessment of the degree of unsaturation of the sample or the number of double-bound compounds in the sample. The determined results for the oils are listed in Table 3.

<table>
<thead>
<tr>
<th></th>
<th>HDPE</th>
<th>PP</th>
<th>PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, kg/m$^3$</td>
<td>829 ± 1.0</td>
<td>773 ± 2.0</td>
<td>928 ± 1.7</td>
</tr>
<tr>
<td>Kinematic viscosity, mm$^2$/s</td>
<td>-</td>
<td>2.216 ± 0.03537</td>
<td>1.454 ± 0.05828</td>
</tr>
<tr>
<td>Iodine number, g/100 g sample</td>
<td>70 ± 1.0</td>
<td>41 ± 0.8</td>
<td>77 ± 0.7</td>
</tr>
<tr>
<td>Ash content, %</td>
<td>0.019 ± 0.0003</td>
<td>0.017 ± 0.0003</td>
<td>0.019 ± 0.0002</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>35 ± 0.6</td>
<td>-10 ± 0.0</td>
<td>-</td>
</tr>
</tbody>
</table>

The data in Table 3 show that PS oil has the highest density, and PP has the lowest. The density of petroleum products depends on their chemical composition. Since hydrogen has a much lower atomic mass than carbon, hydrocarbons with more hydrogen atoms and fewer carbon atoms in their molecules have a lower density. These hydrocarbons have a lower boiling point and a higher heating value. As for one of the most important indicators of the fluidity of fuels and oils, kinematic viscosity, PS oil has the lowest viscosity, and
HDPE oil could not be determined because of its high pour point (35 °C). PP has a pour point of −10 °C, while PS oil was not solidified at −30 °C (lower measurement limit). In the literature, a pour point of −64 °C is given for PS oil [12].

The iodine value is determined in the literature [22,28] only for biodiesel or biooils. Mineral diesel has only a very small iodine value, so probably for this reason, this characterization method is not used for pyrolysis oils. The iodine number is used to determine the number of double bonds in an olefin, which reflects the oxidation stability of the biodiesel [24]. The highest iodine number was measured for PS oil and the lowest for PP oil. Since, to the authors’ knowledge, no iodine numbers are determined for pyrolysis oils, only a comparison with iodine numbers from the literature on bio-oils can be made here. Accordingly, the values of the iodine numbers lie between those of palm oil and mahua oil [29].

To refine the results of the iodine number measurements, a study of the oxidation stability of the oils was performed. In addition, the flash point and heating value of the oils were measured; the results are shown in Table 4:

### Table 4. Results of oxidation stability, heating value, and flash point of plastic pyrolysis oils.

<table>
<thead>
<tr>
<th></th>
<th>HDPE</th>
<th>PP</th>
<th>PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation stability, min</td>
<td>6.09 ± 0.113</td>
<td>9.45 ± 0.187</td>
<td>8.18 ± 0.095</td>
</tr>
<tr>
<td>Calorific value, MJ/kg</td>
<td>46.99 ± 0.392</td>
<td>45.84 ± 0.148</td>
<td>42.41 ± 0.145</td>
</tr>
<tr>
<td>Flash point, °C</td>
<td>48.2 ± 0.56</td>
<td>51.2 ± 0.40</td>
<td>37.2 ± 0.36</td>
</tr>
</tbody>
</table>

Comparing these results with the previously determined iodine number values, it can be seen that the measured properties of PP oil (oxidation stability and iodine number) correlate with each other and indicate that this oil is more stable under environmental influences than the others.

HDPE oil has the highest calorific value of 46.99 MJ/kg (see Table 4), while PS oil has the lowest calorific value of 42.41 MJ/kg, which is consistent with the literature [26].

The flash point results in Table 4 show that PS oil is the most dangerous oil, especially during the summer season, since its flash point is only 37.2 °C. This trend is again consistent with the literature [11,27].

3.3. Atmospheric Distillation of Pyrolysis Oils

Atmospheric distillation is one of the most commonly used physical treatments of pyrolysis oils, separating the oil into fractions with different boiling points. The fractional composition of pyrolysis oils is shown in Figure 2.
Figure 2 clearly shows that the fractional composition of the pyrolysis oils differs considerably between the different plastics. For example, PS oil consists of more than 60% of the gasoline fraction, while PP oil consists of almost 50% of the diesel fraction (compounds boiling in the temperature range 190–320 °C). Distillation of 100 mL of HDPE oil yielded only 8 mL of the gasoline fraction and 22 mL of the diesel fraction.

During atmospheric distillation, the temperature and the amounts of liquid obtained were measured. In particular, the temperature of the gasoline fraction of the PS oil was constant in a range of 140 to 150 °C. Almost 67 mL of distillate was obtained. Styrene is known to boil at 145 °C, so it can be assumed that a styrene fraction was obtained in that temperature range.

3.4. Investigation of the Properties of Distillates

After distillation of the oils by atmospheric pyrolysis, during which the gasoline and diesel fractions were separated, the properties of these fractions were studied, and their values are listed in Table 5.

| Table 5. Properties of gasoline and diesel fractions of the plastics HDPE, PP, and PS. |
|---------------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
|                                  | HDPE               | PP                  | PS                  | HDPE               | PP                  | PS                  |
| Density, kg m⁻³                  | 753 ± 1.0          | 791 ± 1.7           | 723 ± 1.0           | 794 ± 1.7          | 902 ± 1.0           | 943 ± 1.0           |
| Kinematic viscosity (40 °C), mm² s⁻¹| 0.962 ± 0.0098    | 2.745 ± 0.0575      | 0.573 ± 0.0161      | 4.183 ± 0.0210     | 0.713 ± 0.0271      | 2.139 ± 0.0694      |
| Oxidation stability, min         | 4.18 ± 0.072       | 16.47 ± 0.185       | 8.53 ± 0.070        | 23.5 ± 0.361       | 2.5 ± 0.046         | 11.23 ± 0.080       |
| Calorific value, MJ/kg           | 46.39 ± 0.062      | 46.32 ± 0.021       | 45.60 ± 0.202       | 45.53 ± 0.139      | 42.27 ± 0.061       | 42.26 ± 0.075       |
| Flash point, °C                  | 44.2 ± 0.52        | 51.1 ± 0.26         | 49.6 ± 0.50         | 55.8 ± 0.36        | 28.2 ± 0.35         | 34.2 ± 0.26         |
| Iodine number, g/100 g samples  | 74.0 ± 0.46        | 54.0 ± 0.56         | 57.0 ± 0.46         | 33.5 ± 0.36        | 87.0 ± 0.26         | 64.0 ± 0.44         |
| Pour point, °C                   | −5 ± 0.0           | 6 ± 0.6             | −29 ± 0.0           | −25 ± 0.0          | −                 | −                   |

The iodine determination was carried out to determine the degree of unsaturation of the distillates, i.e., the extent to which they contain unsaturated compounds that cause low oxidation stability. The measurements performed showed that the iodine value of the gasoline fraction is higher than that of the diesel fraction, which means that the gasoline fraction contains more double bonds and is less stable [30]. The lowest iodine value was found for the PP diesel fraction with 33.5 g/100 g sample. The same fraction also showed the highest oxidation stability, indicating that the two tests (iodine value and oxidation stability) complement each other well [31].

The measured values for density, viscosity, flash point, pour point, oxidation stability, and heating value agree well with those reported in the literature, such as [32].

The properties of fractions obtained by atmospheric distillation are similar to those of fuels and are expected to be successfully used in commercial production, as the production of fuels consists of a number of different processes and the use of additional additives that further modify the physicochemical properties of the processed feedstock. The only parameter of distillates that is between 55% and 86% below the requirements for gasoline and diesel fuels is oxidation stability. The low oxidation stability of the oils and distillates is probably due to the high content of unsaturated, double-bonded compounds (alkenes, alkadienes, aromatic compounds), the presence of which was confirmed by NMR spectral analysis of the oils (published in [21,33]) and the iodine values determined. Further experimental studies are required to increase the oxidation stability of the distillates.

3.5. Investigation of Distillates with Additives

To increase the oxidation stability, some of the distillates were mixed with phenolic compounds known to have antioxidant properties. Another part of the distillates was mixed with algal pyrolysis oil, which probably also contains phenolic compounds [34–36] that can delay oxidation processes.
Since there is no single universal antioxidant suitable for stabilizing technical mixtures, four phenolic compounds (phenol, resorcinol, hydroquinone, and pyrocatechol) were first selected and tested for their solubility in the distillates. The solubility test showed that resorcinol and hydroquinone were completely insoluble, phenol dissolved immediately, and pyrocatechol dissolved more slowly than phenol. Then, the concentration of the antioxidant was selected. The studies in [19,37] recommend an antioxidant concentration of up to 0.1 wt%, but no change was observed at this concentration and when the iodine value of the resulting mixture was measured, so the concentration was increased to 0.5 wt%.

Mixing the gasoline and diesel fractions of plastics with phenol and pyrocatechol resulted in 12 mixtures. To assess the effect of the selected antioxidant substances, the change in the iodine value of the mixtures over time was measured. It can be assumed that phenol and its derivatives do not react with iodine [38]. The results are shown in Figures 3–6.

Figure 3. Change in iodine value of gasoline fractions of the different pyrolysis oils + 0.5% phenol over the time.

Figure 4. Change in iodine value of gasoline fractions of the different pyrolysis oils + 0.5% pyrocatechol over the time.
Figure 4. Change in iodine value of gasoline fractions of the different pyrolysis oils + 0.5% pyrocatechol over the time.

Figure 5. Change in iodine value of diesel fractions of the different pyrolysis oils + 0.5% phenol over the time.

Figure 6. Change in iodine value of diesel fractions of the different pyrolysis oils + 0.5% pyrocatechol over the time.

It can be seen that, in contrast to diesel fractions, gasoline fractions have higher iodine numbers. This could be because the gasoline fractions are richer in olefinic hydrocarbons [30]. The low iodine numbers in the figures in the first 6 h compared to the values after about 50 h indicate that the antioxidant additives phenol and pyrocatechol are effective [39]. After about 40–50 h, the iodine numbers increase clearly only for PP pyrolysis oils in the gasoline and, in one case, also in diesel fractions but hardly at all in the case of HDPE and PS pyrolysis oils. This could be due to an interaction between the iodide formed in the reaction with the double bonds and the reaction products from the oxidation of phenol and pyrocatechol. The peroxides formed during the oxidation of phenol and pyrocatechol can react with iodide to form iodine, which results in an apparently lower iodine number in the back titration. The higher iodine number in the case of PP pyrolysis oil could be caused by other ingredients [40].

To compare the results of the iodine number measurements, the oxidation stability of the additive distillates was measured. In addition, this indicator was measured for algal mixtures containing 5% algal pyrolysis oil. The results obtained are shown in Figure 7.
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To compare the results of the iodine number measurements, the oxidation stability of the distillates was measured. In addition, this indicator was measured for algal pyrolysis oil and commercial diesel blends. The blends were prepared from 20% biodiesel and 80% diesel fuel with the addition of one of the following antioxidants (0.1 wt%): propyl gallate (PG), pyrogallol (PY), tert-butylhydroquinone (TBHQ), dibutylhydroxytoluene (BHT), and butylhydroxyanisole (BHA). The oxidation stability of the mixtures was then measured using the Rancimat method [41]. The studies showed that TBHQ and PG were the most effective antioxidants. They increased the oxidation stability of the mixtures by 34% and 28%, respectively. In contrast, the addition of BHA had virtually no effect on the oxidation stability of the blends. As can be seen from the results, the effect of phenol on the oxidation stability of the blends is similar to that of TBHQ and PG mentioned in this work.

Figure 7 shows that the oxidation stability of the distillates with the phenol additive is the highest in all cases, being most pronounced for PP. The oxidation stability of the gasoline fraction of this plastic (with phenol) is almost 18 min, 49% higher than that of the same fraction without the antioxidant. For the diesel fraction of PP, the oxidation stability of the mixture with phenol is even higher at 32 min. This is an increase of 36% compared to the diesel fraction without phenol. It follows that the influence of the phenol addition on the oxidation stability of the distillates is positive but not sufficient, since the measured values do not meet the minimum requirements for the oxidation stability of the fuels.

The yellow lines in Figure 4 represent the oxidation stability of the fractions without additives. A comparison of the effects of pyrocatechol and algae on the oxidation stability of the blends shows that algal pyrolysis oil improves the oxidation stability of all gasoline fractions (PS 34%, PP 7%, HDPE 46%), while for the diesel fractions, it improves only the oxidation stability of the HDPE distillate (4%). In contrast, the influence of the pyrocatechol additive is less positive: only the oxidation stability of the PS gasoline fraction increased by 24%, while in the other cases, the oxidation stability decreased, especially for the diesel fractions (PS 27%, PP 15%, HDPE 37%). This indicates that pyrocatechol is not suitable as an antioxidant, at least not for the stabilization of HDPE, PP, and PS distillates.

The study of [19] studied the effect of different phenolic antioxidants on biodiesel and commercial diesel blends. The blends were prepared from 20% biodiesel and 80% diesel fuel with the addition of one of the following antioxidants (0.1 wt%): propyl gallate (PG), pyrogallol (PY), tert-butylhydroquinone (TBHQ), dibutylhydroxytoluene (BHT), and butylhydroxyanisole (BHA). The oxidation stability of the mixtures was then measured using the Rancimat method [41]. The studies showed that TBHQ and PG were the most effective antioxidants. They increased the oxidation stability of the mixtures by 34% and 28%, respectively. In contrast, the addition of BHA had virtually no effect on the oxidation stability of the blends. As can be seen from the results, the effect of phenol on the oxidation stability of the blends is similar to that of TBHQ and PG mentioned in this work.

4. Conclusions

The expectation in this study was to obtain a fraction more stable than another. The atmospheric distillation results showed that the PP oil consisted of 52% of the diesel fraction, the PS oil consisted of 67% of the gasoline fraction, and the HDPE oil consisted of 67% of
the waxes and resins. The oxidation stability study showed that the diesel fraction has higher oxidation stability than the gasoline fraction. The highest oxidation stability of 23.5 min was found for the PP diesel fraction, which is almost 2.8-times higher than the PP gasoline fraction. The results of the iodine value measurements only confirm the results of the previous study: the lowest iodine value (33.5 g/100 g sample) was also found for the PP diesel fraction, which means that it contains less unsaturated compounds and, therefore, tends to have a lower oxidation rate and higher environmental stability compared to the other oil fractions.

The results of the iodine number determination of the pyrolysis oils with additives showed that the addition of phenol had a positive effect on the iodine value of the blends prepared from the diesel fractions (the iodine value of the PP diesel fraction decreased by 25% over 130 h), in contrast to pyrocatechol (the iodine value of the PS diesel fraction increased by 29% over 80 h). For the gasoline fractions, the effect of the two antioxidants is similar.

In all cases, the oxidation stability of the blends with the phenol additive is the highest, which is most pronounced for PP. The oxidation stability of the gasoline fraction of this plastic (with phenol) is 17.37 min, 49% higher than that of the same fraction without the antioxidant. In the case of the PP diesel fraction, phenol increases the oxidation stability to 32 min. This is a 36% increase compared to the diesel fraction without phenol. Algal pyrolysis oil improves the oxidation stability of the blends for all gasoline fractions (PS by 34%, PP by 7%, HDPE by 46%), while for the diesel fraction, it improves only the oxidation stability of the HDPE distillate (4%). The addition of pyrocatechol only increased the oxidation stability of the gasoline fraction of PS (24%), while in the other cases, it decreased the oxidation stability, especially for the diesel fractions (27% for PS, 15% for PP, and 37% for HDPE).

Further studies are currently underway for further investigations and characterizations of pyrolysis oils.

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