

Article

Pyrolysis Oils from Used Tires and Plastic Waste: A Comparison of a Co-Processing with Atmospheric Gas Oil

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Abstract: This study aimed to determine the effect of the supplied pyrolysis oils (oils obtained from the pyrolysis of used tyres and the depolymerisation of plastics) on the activity of the hydrosulphurisation catalyst. Each pyrolysis oil was added at 20% weight to a standard feedstock and processed on pilot plant reactors under the set conditions of a commercial unit, including an activated catalyst. Following the catalyst stabilisation, the standard material was changed to the mixture with the pyrolysis oils. The reaction conditions, particularly the reaction temperature, were controlled. The results of the product analyses were compared with the EN 590 standard for evaluating diesel fuel; the hydrogenated mixed fuel meets most requirements. Only the density, flash point, distillation curve and lubricity have minor deviations, which could be adjusted by treating the sample before or after hydrogenation. The properties of the products, in terms of the low-temperature properties, were also investigated. The tyre-derived pyrolysis oils showed improved low-temperature properties, possibly due to the higher levels of the aromatic hydrocarbons. The pyrolysis oil obtained from the depolymerisation of the plastics was found to be more suitable for use in refineries without substantially impacting the existing technologies. For the tyre-derived pyrolysis oils, higher reaction temperatures were required for processing, which could affect the catalyst operation.

Keywords: pyrolysis oil; used tyres; plastic; hydrosulphurisation; alternative fuel components



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1. Introduction

In an effort to reduce the dependence on fossil fuels and to create a circular economy, suitable energy sources, especially those derived from waste materials, are being sought. Plastic goods are being manufactured extensively; additionally, the automobile industry requires the production of tyres (and rubber in general). Therefore, problems associated with the disposal of tyres and plastic waste must be considered, as they continue to increase. Studies have been conducted on the recycling of plastic and rubber waste to obtain a valuable substitute, as a primary source for the production of monomers and fuels. The recycling of plastics and tyres (rubber in general) has long been known and is constantly evolving [1–3]. However, most waste from plastic and used rubber is not suitable for recycling and is therefore incinerated in municipal waste incinerators [4].

Tyres have a relatively high calorific value ($30 \text{ MJ} \cdot \text{kg}^{-1}$), and high energy levels can be obtained from their combustion. In cement plants, tyres are typically disposed of through combustion. The material utilisation of discarded tyres is the most environmental-friendly way to use a tyre, as it solves the problems of where to use the tyre and to prevent the wastage of limited raw materials. The tyre contains rubber, textiles, steel wires, and other additives. All of this must be separated during recycling so that the obtained materials are as clean as possible. First, the tyres are crushed into so-called chips, which then continue to the recycling line, where they form granulates. The steel parts are separated by strong magnets, and the textile fibres are sucked out. This process is not easy and requires a relatively good technique. However, once everything is separated, a lot of material is

generated that can be used further. The steel wires travel further to blast furnaces, the textile fibres are used for sound insulation products, and rubber can be used, for example, to produce paving, insulation boards, shock absorbers, or various surfaces [5,6].

The pyrolysis processing of rubber and plastic waste can be used for fuel production. Pyrolysis is the thermochemical decomposition of organic matter in the absence of oxygen. The material is heated above the thermal stability limit of the organic compounds. The main pyrolysis products include semi-coke, liquid pyrolysis oil, and pyrolysis gas. Their ratio can be adjusted by checking the pyrolysis parameters: temperature, pressure, heating rate, and residence time of the products in the reaction space [5].

The pyrolysis oil obtained from tyres is dark and viscous, with a pungent smell, containing BTX and PAH, with high concentrations of sulphur and nitrogen substances and with solid impurities [6]. Therefore, pyrolysis is being continuously modified to improve the properties of the pyrolysis oils from used tyres; this helps in recycling used tyres and also presents an alternative for fuel production. Studies have investigated the pyrolysis of waste tyres with respect to the yield of the liquid product and its hydrodesulphurisation with the help of several catalysts. The physical and chemical properties of the pyrolysis oil alone, mixed with diesel and pure petroleum diesel with EN 590, were compared and, for the most important parameters, the fuel obtained from the pyrolysis of the used tyre was similar to diesel fuel [7]. Using a test engine, diesel and diesel with a 10% volume of tyre oil were compared; combustion, engine power, and exhaust emissions were monitored experimentally. The mixture of diesel and tyre oil was suitable for use in diesel engines [8]. The hydrotreatment of oil from the pyrolysis of passenger car- and van-tyres requires relatively strict conditions to improve the properties. However, even after refining, adding the pyrolysis oil to the motor fuels was not recommended; instead, its addition to the fuel oils, as potential alternative fuels, was suggested [7,9]. The properties of pyrolysis oil from tyres, including the possible modifications, and their effect on the combustion engine and exhaust gas emissions, have been well summarised [10,11].

The properties of pyrolysis oil from plastics are not very different from those of the raw materials processed in refineries; however, the input raw materials may contain chlorinated substances and high levels of nitrogenous substances, which can negatively affect further processing. The higher the quality of the input material, the higher the quality of the pyrolysis oil. If it is possible to maintain stable reaction conditions, the homogeneous pyrolysis oil is produced, for which it is easier to find an application. Plastic pyrolysis can thus be divided into several parts, according to the input material, such as polystyrene [12], polypropylene [13], low- and high-density polyethylene [14,15], polyethylene terephthalate, and polyvinyl chloride (PVC). Particularly, PVC pyrolysis is expected to have a high chlorine concentration, and directly using the liquid PVC pyrolysis product in refineries, can be difficult. For example, LDPE can be used as an alternative solvent for asphalt [16]. The characterisation of pyrolysis oils from plastic for use as fuel has recently been investigated. Similar to the use of the pyrolysis oil from tyres, using pyrolysis oils from plastic as fuel for diesel engines was investigated [17,18]. The effect of these oils on the performance of the combustion engine and emission composition was studied. The addition of pyrolysis oil from plastics and nanocatalysts improved combustion in a diesel engine and reduced the composition of hydrocarbon and CO₂ emissions. NO_x emissions were reduced to a smaller degree [19–21].

Refineries are already modifying their technologies for the future processing of various pyrolysis oils. Primarily, pyrolysis oils are considered as additional components to the already finished fuel or as components for co-processing with the least possible impact on the existing technologies. The oil hydrodesulphurisation unit is one of the main processes among the oil pyrolysis processes, therefore, how the oil might affect this technology, is monitored [22,23]. Due to the available amount of materials of this type, it is reasonable to consider co-processing with the standard raw material on the existing technologies. However, none of the above mentioned research studies address the direct impact of co-processing on operating conditions, or the resulting quality, including the possible

modification of the final product, arising with the use of these two different materials. That is why this research article addressed this issue, with the aim of simulating the operating conditions as closely as possible, including the maximum estimated addition of the pyrolysis oils and their mutual comparison.

This work compares the effect of adding pyrolysis oil from the plastic depolymerization (PE + PP) and from the pyrolysis of waste tyres on real feedstock material, on the same industrial hydrosulphurisation catalyst under real operating conditions. The effect of adding pyrolysis oils on the reaction conditions, the quality of the final product, and the activity of the desulphurisation catalyst used in refineries, was monitored.

The co-processing of the pyrolysis oils from the pyrolysis of used tyres and the depolymerisation of plastics can be carried out using existing hydrotreating technologies. In the case of processing pyrolysis oil from tyres, a faster deactivation of the catalyst can be observed in the long term. The quality of the products depends on the quality of the input raw materials. A comparison with EN 590 shows that products meet this standard in most values. At points where there is no agreement, the products can be modified by the appropriate dosing of additives. In this case, the additive additions were tested to ensure suitable low-temperature properties, and the co-processing of the products of pyrolysis oils meet the requirements for transitional diesel. So, they can be used in the spring, summer and autumn.

2. Materials and Methods

2.1. Materials

Straight run gas oil (SRGO), obtained from the atmospheric distillation of Russian Export Blend (REB) crude oil was used as a standard feedstock for co-processing. Two types of pyrolysis oil were added at 20 wt.% to the SRGO. The pyrolysis oils from tyre pyrolysis (POT) and from the depolymerisation of plastics containing PE and PP (POP), were used. The pyrolysis oils were supplied by external companies and were used as received, without additional modifications. Their distillation curves are shown in Figure 1 and their properties are listed in Table 1.

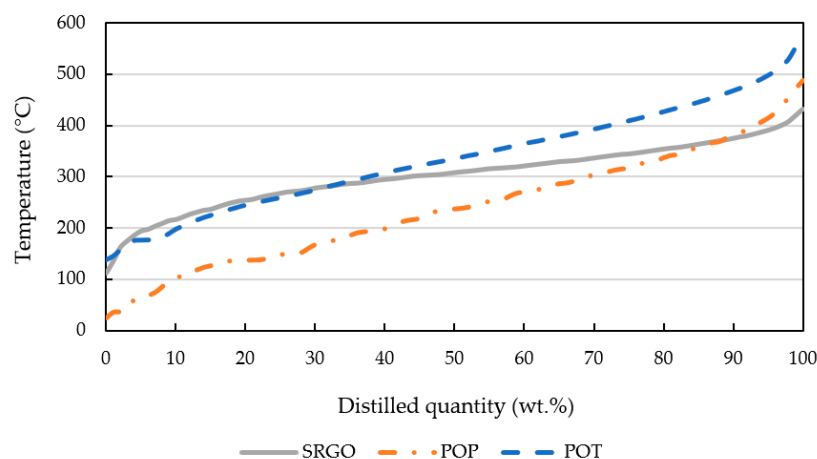


Figure 1. Distillation curves of the used feedstock.

As can be seen from the distillation curves (Figure 1), the POP contains many light fractions, with the start and end of the distillation at 24 °C and 487 °C, respectively. The distillation curve of the SRGO begins at 111 °C and ends at 432 °C. The heaviest feedstock, in this case, was the POT sample, with the distillation curve starting and ending at 137 °C and 574 °C, respectively. The content of the middle distillates (diesel) range (180–360 °C) in each feedstock is as follows: the standard feedstock, POT, and POP contain approximately 87 wt.%, 51 wt.%, and 52 wt.%, respectively.

Table 1. Analytical characterisation of the used pyrolysis oils.

Parameter	POT	POP
Density at 15 °C (kg·m ⁻³)	938.9	779.5
Refractive index at 20 °C	1.5246	1.4352
Colour ASTM D1500	>9.0	2.1
Sulphur content (mg·kg ⁻¹)	10,900	5.5
Nitrogen content (mg·kg ⁻¹)	4733	819
Carbon content (wt.%)	88.3	87.4
Hydrogen content (wt.%)	11.2	12.6
Chlorine content (mg·kg ⁻¹)	78.7	23.9
C/H ratio	7.9	6.9
Flash point (°C)	94	<21
Water content (mg·kg ⁻¹)	335	123
Non-aromatics (wt.%)	70.6	95.3
Mono-aromatics (wt.%)	20.9	3.3
Di-aromatics (wt.%)	1.7	1.1
Poly-aromatics (wt.%)	6.8	0.3

Table 1 compares the basic properties of the supplied pyrolysis oils. The POT and POP oils differ substantially. Both pyrolysis oils differ markedly in water content; POT contains 335 mg·kg⁻¹, which is twice that of the standard feedstock and more than twice that of the POP. Higher contents of sulphur, nitrogen, and chlorine can be a possible problem during the processing of the POT in a hydrogenation unit. The limit for the chlorine concentration is then 2 mg·kg⁻¹. Compared to the POP, the POT also contains more aromatics. The processing of the POP oil, in addition to the SRGO, would not necessarily pose a serious problem, given the basic properties set. It is a slightly orange-coloured liquid with low contents of sulphur and water. The flash point for POT and POP are 94 °C and below 21 °C, respectively, according to the standard.

The two starting materials were prepared for the hydrogen refining testing. The basis of both raw materials was the SRGO, which is used in refineries as a standard feed for the hydrogenation of diesel fuel. The raw materials were the SRGO with 20 wt.%, and POT (T) and SRGO with 20 wt.% POP (P). The physical and chemical properties of the SRGO and the mixed raw materials were determined, and are listed in Table 2.

Table 2. Analytical characterisation of the used feedstocks.

Parameter	SRGO	T	P
Density 15 °C (kg·m ⁻³)	853.3	870.4	838.5
Refractive index 20 °C	1.474	1.484	1.466
Colour ASTM D 1500	1.1	2.7	1.3
Sulphur (mg·kg ⁻¹)	11,000	10,980	8801
Nitrogen (mg·kg ⁻¹)	233	1133	350
Carbon (wt.%)	86.8	87.1	86.9
Hydrogen (wt.%)	13.1	12.7	13.0
Chlorine (mg·kg ⁻¹)	0	15.7	4.8
Water (mg·kg ⁻¹)	169	202	160
Flash point (°C)	88	94.0	49.0
C/H ratio	6.6	6.9	6.7
Other (wt.%)	66.4	67.2	72.2
Mono-aromatics (wt.%)	21.7	21.5	18.0
Di-aromatics (wt.%)	11	9.1	9.0
Poly-aromatics (wt.%)	0.9	2.1	0.8

The influence of adding 20 wt.% of the pyrolysis oil (POP and POT) can be seen from the properties of the feedstocks (Table 2). Unlike the SRGO, both mixed raw materials contain chlorine, which could be problematic, due to its corrosive properties [24]. The

flash point is in accordance with the distillation curve of all of the input materials, and was found to be 88 °C, 94 °C, and below 49 °C, for the standard injection, T, and P, respectively, according to the standard.

2.2. Methods

The atmospheric distillation test was performed according to ASTM D 86, using a Tanaka AD-6 apparatus. The chlorine determination was performed according to ASTM D 4929. The colour was assessed on a Lovibond PFX880/P instrument, according to ASTM D 1500. The methods for determining the cetane number are prescribed by the technical standards ASTM D 613. Nitrogen was measured on a Trace SN Cube instrument, according to ASTM D 4629. A Trace SN Cube instrument, according to ASTM D 5453, was used for the determination of sulphur. The density was measured using the digital density meter DA 645 from KYOTO ELECTRONICS, according to ASTM D 4052. The lubricity is a measurement for oil or fuel oil lubrication and considers a high-frequency piston device, according to ISO 12156-1. The oxidation stability determination was performed on a rancimat instrument, according to EN 15751. The flash point was determined, according to ISO 2592. The water content, by the K. Fischer method—coulometric titration with a bi-ampere endpoint indication on a Mettler DL37-KF Coulometer, according to ASTM D 4928. The chromatography of the saturated hydrocarbons and the aromatics in medium-boiling fractions (diesel fuel) was performed on a 1260 INFINITY AGILENT TECHNOLOGY, according to IP 391. The simulated high temperature distillation (SIMDIST) was performed on a HP 7890 chromatograph from Hewlett Packard, according to D 2887. The filterability value on a cold filter (CFPP—Cold Filter Plugging Point), was determined on the ISL FPP 5Gs device, in accordance with EN 116. The metal content qualitative analysis was performed on an inductively coupled plasma optical emission spectrometry instrument—ICP—OES, according to ASTM D7303-17. The determining pore volume distribution of catalysts were made, according to ASTM D4284-12. A Raman scattering microscope DXR from ThermoFischer Scientific (Waltham, MA, USA) was used for the Raman analysis.

The WABT is the average temperature of each catalytic bed in between two temperature indicators, and T^{in} and T^{out} are the inlet and outlet temperatures in each catalytic bed, respectively. The WABT was calculated according to the following Equation (1).

$$\text{WABT}_i = \frac{T_i^{\text{in}} + 2T_i^{\text{out}}}{3} \quad (1)$$

2.3. Experimental Unit

The test unit had two identical down-flow reactors with the co-current flow of raw material and gas flow labelled 909-203 and 909-210. The scheme for one reactor is shown in Figure 2.

Unit 909 was equipped with two identical R203 and R210 reactors with a scrubbed catalyst bed. Both reactors could be used simultaneously and independently.

The reactors were equipped with an insulating ceramic jacket with heating elements in three heated zones. The temperatures of the individual zones are monitored by external thermocouples TI 1, TI 2, and TI 3, which are located laterally on the outer wall of the reactor and measure the reactor surface temperature in a given temperature zone. A thermo-probe containing six internal thermocouples (TI 4 to TI 9) passed through the centre of the reactors. Each zone had two fixed internal thermocouples to maintain the temperature inside the catalytic layer, at the desired level. In this case, the top section was controlled by TI 5 (the second thermocouple from the top of the reactor), the middle section by TI 6 and TI 7, and the bottom section by TI 8 (the penultimate measured point in the feed flow direction).

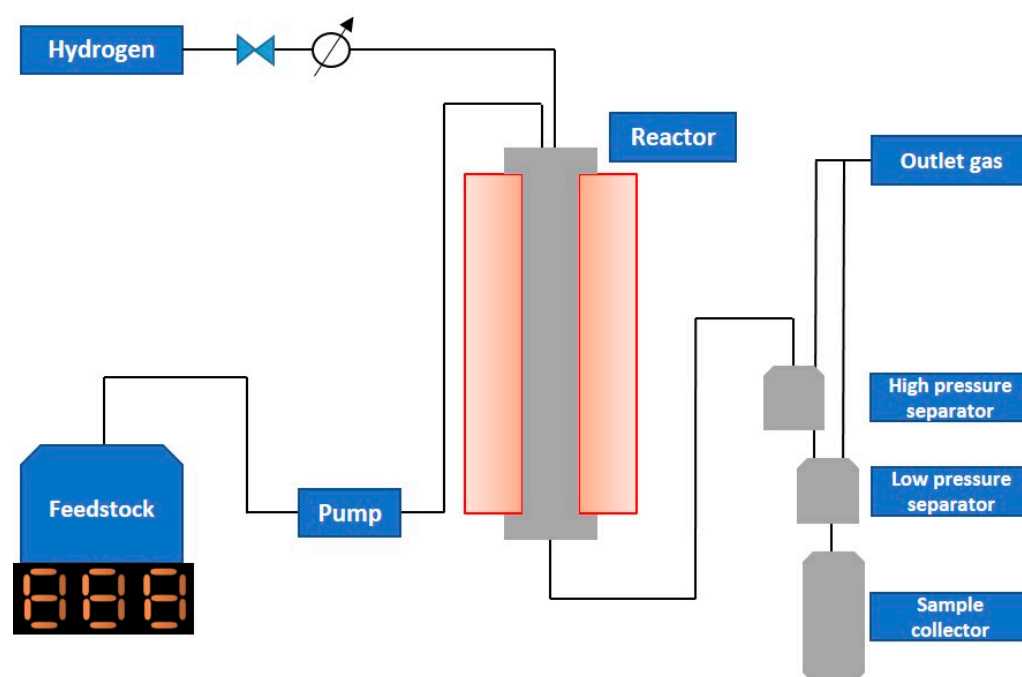


Figure 2. Flow Unit 909-203.

The used feedstock was injected by the ROHS pump from the weighed container. The flow of the reaction gas (hydrogen) was controlled by a BROOKS mass regulator and a reactor pressure was maintained by a TESCOM pressure regulator. The feedstock was injected into, from the top of the reactor, and hydrogen was mixed with the feedstock at the inlet of the reactor.

All experiment parameters (required reaction conditions) were monitored using SpecView software.

2.4. Catalyst Bed

To ensure the adequate hydrodynamic criteria and the catalytic bed isothermal profile (considering the length of the reactor), a total of 100 mL of hydrodesulphurisation CoMo/ γ -Al₂O₃ catalyst, in the original shape of a trilobe with a diameter of 1.3 mm and a length of 4 mm, was added to each of the two reactors. Silicon carbide (SiC) was used as a diluent. Silicon carbide fills the gaps in the catalyst bed to ensure the proper hydrodynamics and a better contact of the feedstock with the catalyst.

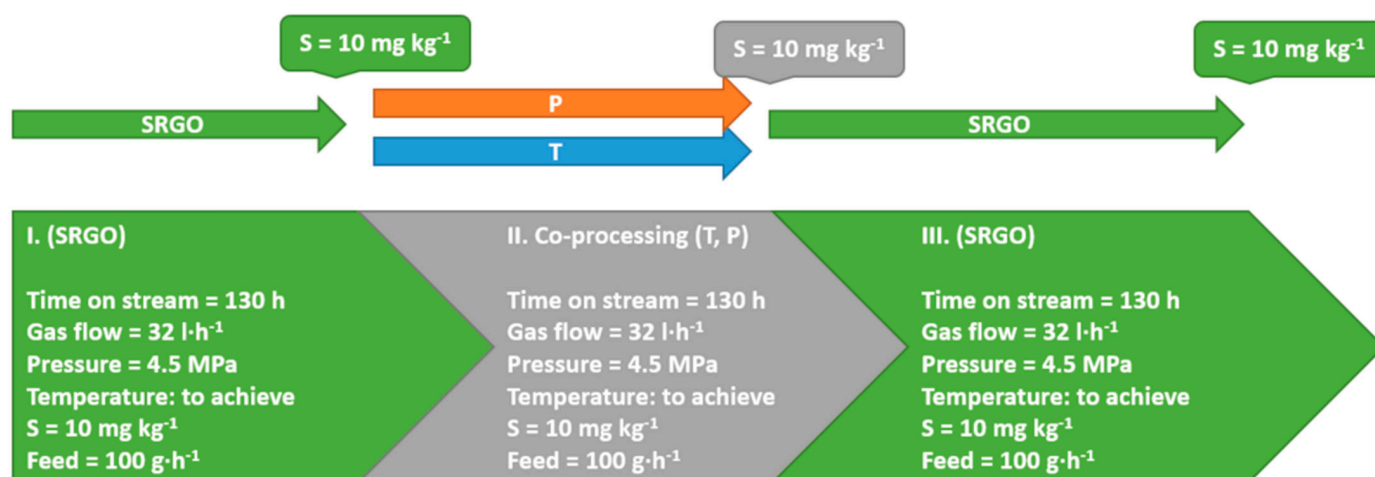
The top layer of the reactor charge serves to preheat the reaction mixture to form 140 mL of SiC of 1–2 mm. The catalyst bed consisted of a single layer of 20 mL of the SiC catalyst mixture (0.1 mm size) in a 1: 3 volume ratio, then a layer of 15 mL of a 1:2 mixture of the SiC/catalyst (0.1 mm). The last layer of the catalyst contained 180 mL of the catalyst/SiC mixture of about 0.1 mm in a 1:1 ratio. The lower layer consists of the inert compound (SiC in sizes 1–2 mm and 2–3 mm) for the fix of the catalyst bed in the isothermal area. The loading diagram is shown in Table 3.

Table 3. Loading diagram.

Glass Wool SiC 1–2 mm (140 mL)
Glass wool Catalyst + SiC 0.1 mm 5 mL + 15 mL (1×) 5 mL + 10 mL (1×) 10 mL + 10 mL (9×)
Glass wool SiC 1–2 mm Glass wool

2.5. Operating Conditions

The process operating conditions are shown in Figure 3 and Table 4. The operating conditions for testing the addition of the pyrolysis oils are similar to the operating conditions used in the actual operation of the hydrosulphurisation units.

**Figure 3.** Flow sheet diagram.**Table 4.** Properties of the testing.

Parameter	Values
Feedstock	SRGO, T, P
Service and wash gas	Technically pure H ₂
Reaction temperature (°C)	350–382
Pressure H ₂ (MPa)	4.5
Feed spraying (g·h ⁻¹)	100
Gas flow (l·h ⁻¹)	32
Sampling (h)	After 4
Washing samples (l·h ⁻¹)	200

I. The Condition—SRGO feed under the reaction conditions of Table 4 and the temperature adjustment to give a sulphur concentration in the final product in the level of 10 mg·kg⁻¹. This condition is identical for both reactors. Hereinafter referred to as I.

II. The Condition—Co-processing of T on R203 and P on R210. Subsequently, the temperature adjustments result in a sulphur content of 10 mg·kg⁻¹. Hereinafter referred to as II.

III. The Condition—Change the feed of the raw materials to the SRGO again, to compare the effect of adding the individual pyrolysis oils on the catalyst activity. Hereinafter referred to as III.

3. Results

The results are focused on the reaction temperature as one of the indicators of the activity of the hydrodesulphurisation catalyst. The product properties for each pyrolysis oil and for each condition were evaluated. The properties of the pyrolysis oil co-processing products are compared with the EN 590 standard for evaluating the diesel properties. Finally, an analysis of the catalyst after the experiment was performed. The processing of the pyrolysis oil from tyres is denoted by 'T' and the processing of oil from the depolymerisation of plastics, by 'P'.

3.1. Temperature

Due to the dependency of the sulphur content of the products on the reaction temperature, the temperature distribution inside the reactor had to be monitored, using the temperature profile inside the catalytic bed. An example of a temperature profile for the co-processing is shown in Figure 4.

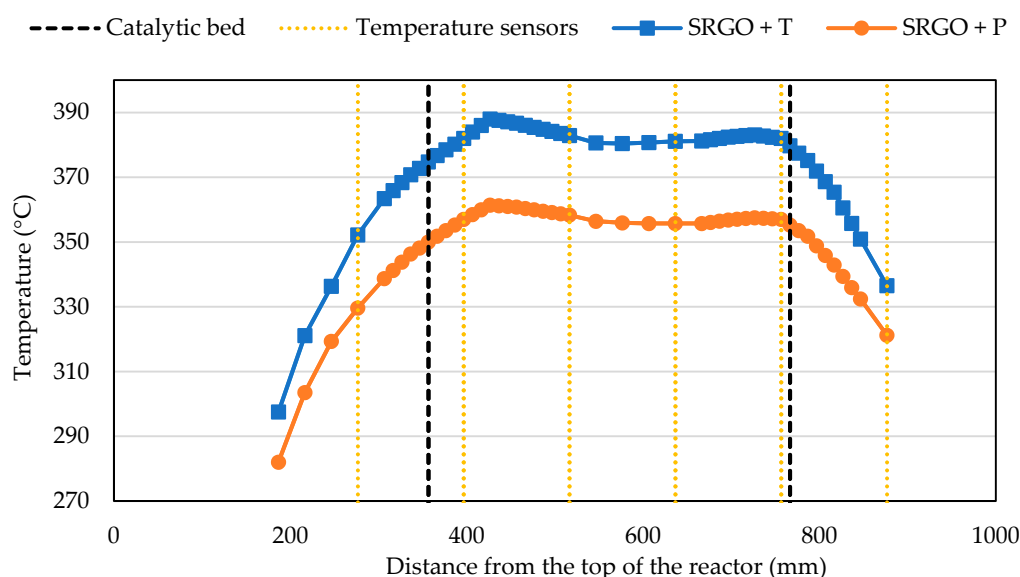


Figure 4. Temperature profile for the Co-processing.

Figure 4 shows the temperature profile in both reactors when injecting the mixed raw materials. The black vertical lines show the start and end of the catalytic bed, and the vertical yellow lines show the temperature sensors inside the catalytic bed. By moving these sensors (temperature probes) and marking the temperatures, the temperature profile was determined. To calculate the WABT (according to Equation (1)), the location of the catalyst bed in the reactor had to be determined before each experiment, and the weight of the catalyst was also recorded for each experiment.

Table 5 shows the average catalyst bed temperature for each condition, which resulted in a sulphur content of $10 \text{ mg} \cdot \text{kg}^{-1}$ in the products. The temperature is consistent with the WABT calculation when the catalyst bed temperature difference does not exceed 1°C . For the condition I, the difference in the WABT between the reactors was 0.4°C . When processing the feedstock containing 20 wt.% of the pyrolysis oils in the standard feed (condition II), the temperature difference between the reactors was 25.1°C . This is due to the higher content of nitrogen, sulphur, and aromatic substances in the feedstock (Table 2). These substances act as catalytic poisons, reducing the efficiency of the catalyst, or utilising part of the hydrotreating capacity of the reactor to the detriment of the hydrodesulphurisation. Thus, the catalyst must necessarily operate at higher temperatures. In condition III, the temperature of the reactor (T) was increased by 3°C , compared to condition I, to regain the final sulphur content of $10 \text{ mg} \cdot \text{kg}^{-1}$. On the reactor (P), the difference between the conditions I and III, was 2°C . These changes suggest that the catalyst deactivation was indeed

only partial (2 °C for P and 3 °C for T) and that the decrease in hydrodesulphurisation activity is due to the competitive reactions to the process.

Table 5. Value of the WABT for each condition.

WABT (°C)	T	P
I	357.3	357.7
II	382.3	357.2
III	360.3	359.7

3.2. Product Yields and Quality

Based on the test results, the mass balance of the individual fractions from the product was also calculated, and is shown in Table 6.

Table 6. Mass balances of the products during the processing of the pyrolysis oils.

Balance	T	P
Consumption H ₂ (wt.%)	0.64	0.64
Diesel fraction (wt.%)	90.08	88.60
Fraction C ₅ –150 °C (wt.%)	7.42	9.11
C ₁ –C ₄ fraction (wt.%)	1.31	1.39
H ₂ S (calculated) (wt.%)	1.20	0.92

Table 6 shows the mass balance of products in the processing of pyrolysis oils. The yields of the gasoline fraction are substantially different here, due to the different volumes of these fractions in the original samples of the individual pyrolysis oils. Figure 5 shows the comparison of the distillation curves of the products, according to the yields. When comparing the distillation curves of both hydrogenation products, in terms of the yield of the individual fractions, smaller differences can be seen only at the lower boiling points.

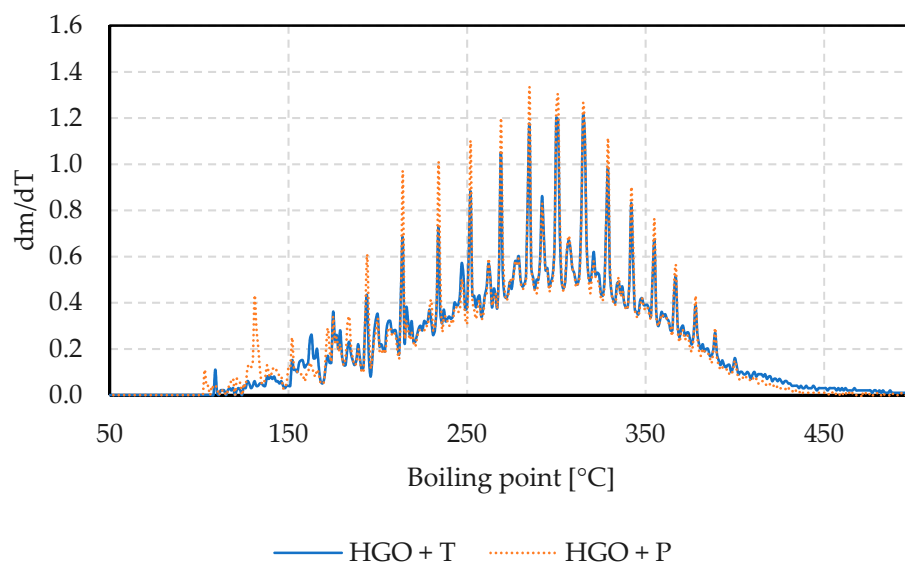


Figure 5. Comparison of the distillation curves of the products, according to the yields.

From the samples obtained from hydrotreating, the representative samples were selected, and the average values were obtained for the given reaction condition. These samples were subjected to a detailed characterisation (Table 7).

Table 7. Average values of the products obtained under each condition.

Parameter	I. (T)	I. (P)	II. (T)	II. (P)	III. (T)	III. (P)
Density 15 °C (kg·m ⁻³)	835.4	835.8	846.5	826.6	834	835.4
Refractive index 20 °C	1.4619	1.4621	1.4689	1.4574	1.4625	1.4619
Colour ASTM D 1500	0.5	0.5	1.6	0.5	0.5	0.5
Sulphur (mg·kg ⁻¹)	9.9	9.9	10.0	10.0	10.4	9.9
Nitrogen (mg·kg ⁻¹)	1.4	2.6	22.6	2.1	3.9	2.7
Carbon (wt.%)	86.6	86.6	86.6	86.5	86.5	86.3
Hydrogen (wt.%)	13.9	13.9	13.4	14.2	13.9	13.9
Chlorine (mg·kg ⁻¹)	<1	<1	<1	<1	<1	<1
Other (wt.%)	75.6	75.3	68.8	77.5	73.7	73.9
Mono-aromatics (wt.%)	22.4	22.5	26.6	20.6	23.8	23.0
Di-aromatics (wt.%)	1.9	2.1	4.0	1.8	2.4	2.9
Poly-aromatics (wt.%)	0.1	0.1	0.6	0.1	0.1	0.2

The composition of the products did not differ substantially between conditions I and III. During the co-processing of pyrolysis oils for T and P, the marked differences can be seen mainly in the density, the colour, according to ASTM, the nitrogen content, and the contents of mono-aromatics/others. These data are consistent with the values for the feedstocks and differ primarily in the composition of the two pyrolysis feedstocks. For a comparison with the EN 590 standard, the representative samples from the coprocessing were further analysed, as shown in Table 8.

Table 8. Comparison of product values with EN 590.

Properties	Min	Max	T	P
Cetane number	51	-	52.9	58.3
Cetane index	46	-	50.9	58.4
Density 15 °C (kg·m ⁻³)	820	845	846.5	826.6
Polycyclic aromatic hydrocarbon content (wt.%)	-	8.0	4.6	1.9
Sulphur content (mg·kg ⁻¹)	-	10	10	10
Flash point (°C)	over 55	-	70	52
Carbonisation residue (based on 10% of the distillation residue) (wt.%)	-	0.30	0.04	<0.01
Ash content (wt.%)	-	0.01	0.01	0.01
Water content (mg·kg ⁻¹)	-	200	61	17
Total impurities (mg·kg ⁻¹)	-	24	4.5	1.0
Fatty acid methyl ester content (FAME) (vol%)	-	7	-	-
Oxidation stability (hour)	20	-	68.9	67.3
Lubricity (µm)	-	460	572	579
Viscosity 40 °C (mm ² ·s ⁻¹)	2	4.50	3.91	3.91
Distillation				
Distills at 250 °C (vol%)	-	<65	24	28
Distills at 350 °C (vol%)	85	-	88	92
95% vol (°C)	-	360.0	386.7	361.2

In most of the evaluation characteristics for diesel, the products were evaluated after the processing of the addition of the POT and POP. The cetane number, cetane index, polycyclic aromatic hydrocarbon content, sulphur content, carbonation residue, ash content, water content, total impurity content, oxidative stability, and viscosity are satisfactory.

The density determined at 15 °C, according to the EN 590 standard, was met by the product only when it was processed with the POP oil. The density of T was higher by 1.5 kg·m⁻³.

The flash point evaluation is better for products with POT oil, and POP oils were not suitable. Both products did not meet the quality of diesel fuel in terms of the distillation curve, as the products only comply with the distilled volume at 250 °C and 350 °C. For the maximum allowable temperature at 95% vol, the POP and POT products exceeded this value by 1.2 °C and 26.7 °C, respectively.

The lubricity requirement can be met by adding lubricant additives which are added to the diesel fuel as standard, without adding FAME.

Both products met the EN 590 standard for the total impurities.

For using the diesel fuel beyond the summer season, the filterability of the products was determined, according to Table 9, which is also part of EN 590.

Table 9. Climatic requirements for the diesel fuel and the test methods—Mild climate.

Parameter	Unit	Class A	Class B	Class C	Class D	Class E	Class F	Method
CFPP	°C, Max	+5	0	−5	−10	−15	−20	EN 116

The pure SRGO showed the lowest filterability values of all analysed samples after the additives; however, more than 600 mg·kg^{−1} additive would have to be added for this fuel to meet the values for winter class F. In the case of the standard injection with component T, the additive showed favourable low-temperature properties, but the CFPP values were higher compared to the SRGO sample. The SRGO and T processing product met the CFPP values for class D of the transition period. The worst results, that is, the highest values of the CFPP parameter, were observed after processing P; the effectiveness of the used additive was visible only at a concentration higher than 400 mg·kg^{−1}. The dependence of the CFPP on adding the additive, can be seen in Figure 6.

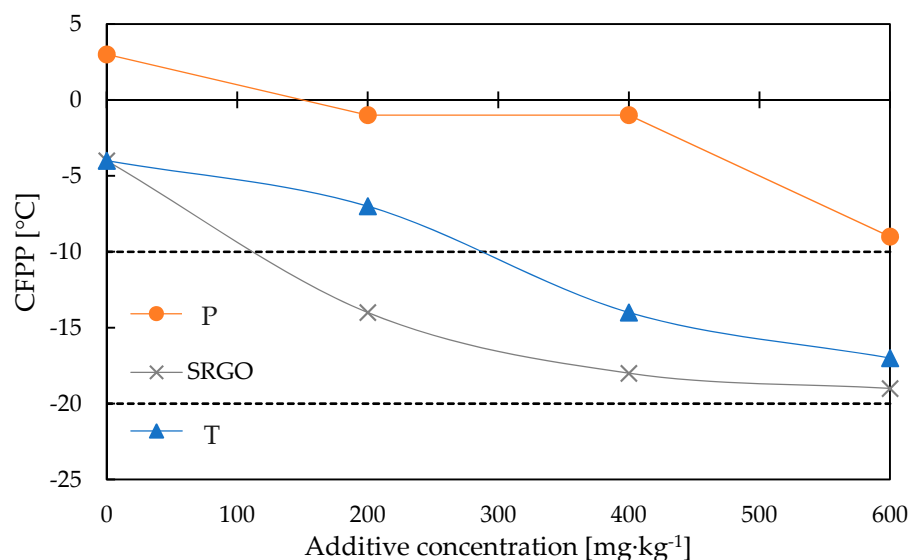


Figure 6. Dependence of the CFPP value on the additive concentration (dashed lines represent the limits of ČSN EN 590 for the transitional diesel (−10 °C) and winter (−20 °C)).

3.3. Catalysts Evaluation

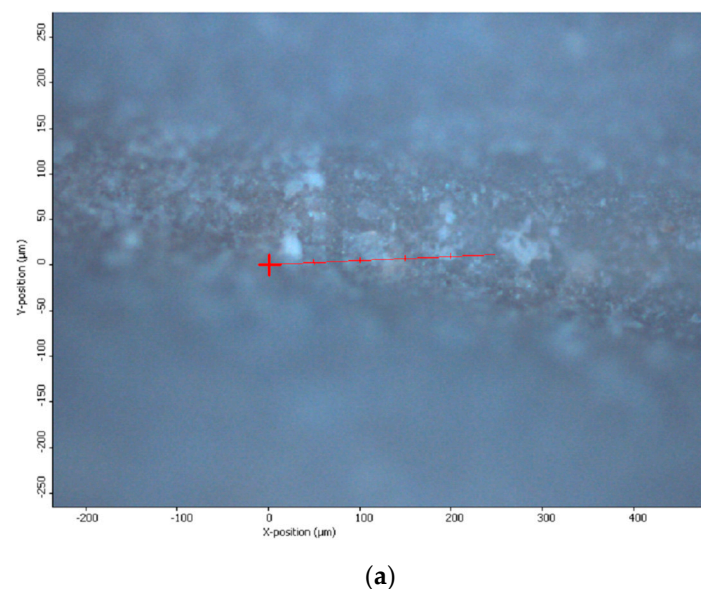
The used CoMo/ γ -Al₂O₃ catalyst was discarded, and after the extraction with cyclohexane, the sulphur and carbon contents were evaluated. The specific surface area of the catalyst and the metal content were also monitored. The resulting values are shown in Table 10.

Table 10. Properties of the catalysts after the hydrogenation of the pyrolysis oils.

Parameters	Fresh Cat.	After T	After P
Al (wt.%)	31.40	32.50	32.80
Ca (wt.%)	0.10	0.05	0.05
Co (wt.%)	2.64	2.73	2.75
Fe (wt.%)	0.06	0.05	0.04
Mo (wt.%)	10.6	10.70	10.80
Na (wt.%)	0.40	0.40	0.40
Ni (wt.%)	0.09	0.10	0.10
P (wt.%)	1.14	1.16	1.19
Si (wt.%)	0.20	0.13	0.13
S (wt.%)	<0.05	12.60	11.10
C (wt.%)	4.97	4.83	5.17
Zn (wt.%)	0.03	0.01	0.01
Total Intrusion Volume	0.367	0.389	0.395
Total Pore Area	168.5	173.0	173.7
Median Pore Diameter (Volume)	9.0	9.5	9.5

Table 10 shows the elemental composition of the catalysts used, which is mostly identical. The sulphur content of the fresh catalyst is low because the fresh catalyst was not activated by the sulphurisation. Following the operation, a higher sulphur content was observed on the catalyst on which P was processed. The same catalyst also showed a decrease in the specific surface area, compared to the catalyst that was used during the processing of T. The obtained differences are within the methods' accuracy.

To compare the homogeneity of the catalyst surface, the samples were evaluated and photographed using a Raman microscope. Figure 7 shows the photographs of the fresh catalyst and the used catalyst after the reaction. According to the Raman microscopy measurements, the catalyst surface can be evaluated as homogeneous. The resulting spectrogram is the average of several measuring points from each catalyst and is shown in Figure 8.

**Figure 7.** Cont.

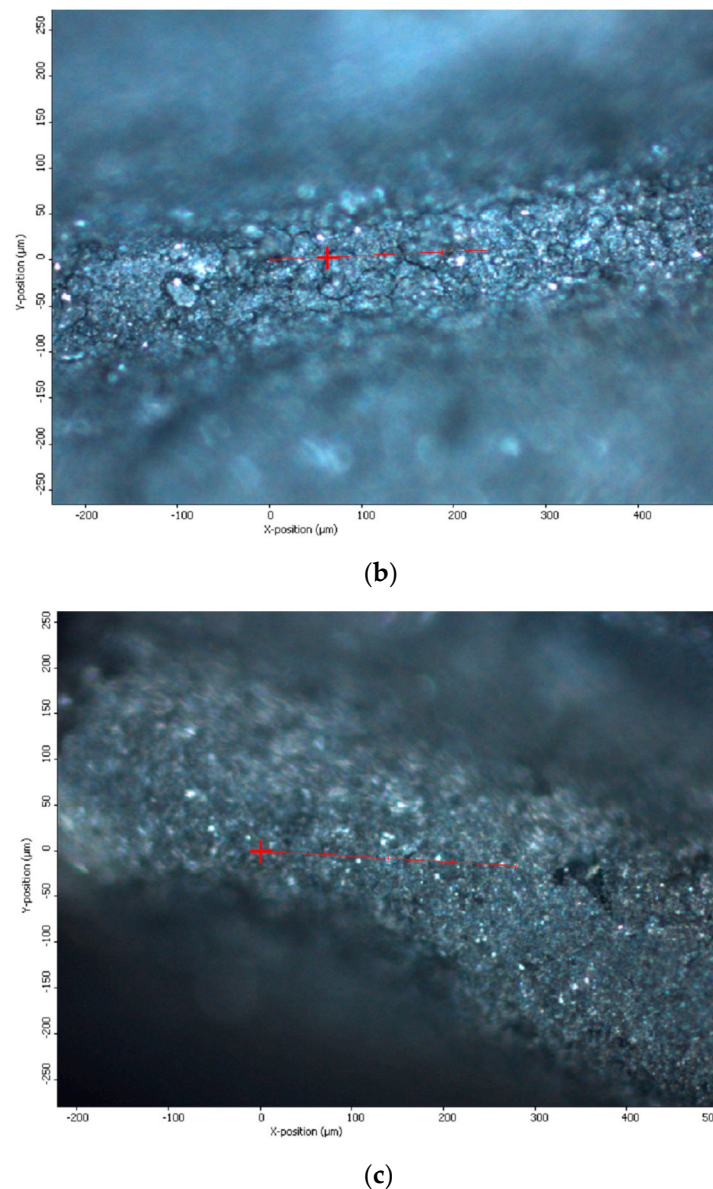


Figure 7. The surface of the catalysts' assessment with the Raman microscopy (a) fresh catalyst, (b) used catalyst after T, (c) used catalyst after P. The red line is the measured area.

Figure 8 compares the Raman spectra of the two used catalysts, and carbon and graphite carbon allotropes were found in their Raman spectra. Both materials can be easily distinguished, according to their Raman spectra, even if they are entirely formed by C-C bonds. The carbon spectrum has several bands and the main band has shifted from a 1350 cm^{-1} D-band to a 1580 cm^{-1} in a G-band. This is because the graphite consists of sp^2 carbon bonds in planar plates in which the energy of the sp^2 bonds is higher than the sp^3 bonds of the diamond. The higher energy of the sp^2 bonds in the graphite pushes the vibrational frequency of the bonds, and thus, their frequency in the Raman spectrum rises to a higher frequency. The presence of the bands in the carbon spectrum suggests that some carbon bonds possess different bond energies because carbon has several possible structures [25,26].

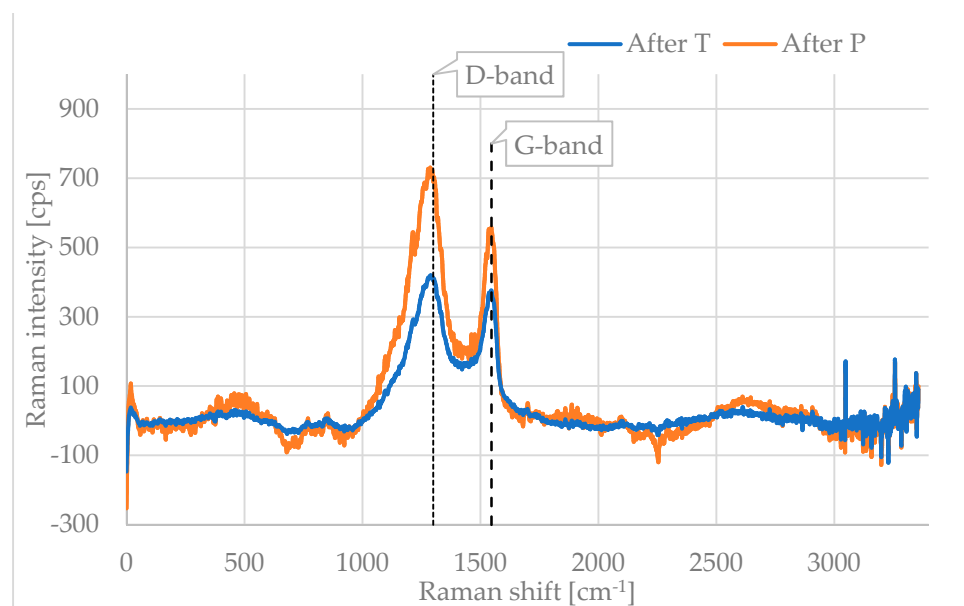


Figure 8. Comparison of the Raman spectra of the used catalysts.

4. Discussion

POP and POT oils were added at 20 wt.% to the commonly used [27] fossil-based feedstock (SRGO) before the hydrodesulphurisation of the middle distillates, and the effect of processing on the activity of the used hydrodesulphurisation catalyst was determined. Attention was also paid to the quality and possible treatment of the selected properties of the products obtained during co-processing, which is an important factor for the overall evaluation [28].

The addition of POT had a more significant influence on the process conditions, due to higher amounts of substances that were hard to process. Compared to the standard feedstock, the temperature at the co-processing stage had to be increased by 24 °C to comply with the sulphur content limit. These differences can be attributed to the high content of the nitrogenous substances, which act on the catalyst as a reversible inhibitor of its activity [29,30]. A strong inhibitory effect can then lead to an overall influence on the HDS kinetics [31], which must be compensated by a higher reaction temperature. This is also exacerbated by the fact that most of the sulphur species in this type of material are bound in the form of less degradable dibenzothiophenes and benzonaphthothiophenes [32]. The mentioned reversible inhibition is also evidenced by the fact that after returning the standard raw material (SRGO) processing, the reaction temperature could be reduced again to a comparable level as before the co-processing. The detected difference in the WABT between step I and III can be attributed to the effect of the spontaneous deactivation of the HDS catalytic system [33]. When processing the raw material by adding the POP, the temperature difference was 0.5 °C, and did not have to be adjusted. This fact is in accordance with the characteristics of the input material, on which a low content of both nitrogen and sulphur compounds is evident. It is also necessary to mention the low content of aromatics, which can also inhibit the HDS reaction [34]. The total temperature difference between the two POs required to meet the maximum permissible sulphur content is then 25 °C. The difference in the hydrodesulphurisation temperature of both raw materials is therefore considerable. Thus, due to the higher operating temperature during the processing of the products from the pyrolysis of tyres, the hydrodesulphurisation catalyst will be deactivated more quickly in the long term. It is also necessary to mention the higher operating cost that would be associated with the processing of such a material.

The evaluation of the products showed substantial differences, especially in the content of the unsaturated aromatics and nitrogenous substances, which were at unacceptable levels

in the POT oil. The products with POP additives were unaffected. The products were also compared with EN 590, and the measured data largely complied with the standard. The unsatisfactory values for the fuel lubricity can be remedied by adding the lubricating additives to the products at the required levels. If the individual distillation sections were processed from each pyrolysis oil, which in this case is in the distillation range of 180–360 °C, the properties, including the density and range, of both the feedstock and the products would be improved in favour of the EN 590. The distillation curve would be more closely aligned with the standard, but in the present work, the POs were processed without any prior modification. Although some scientific works recommend the direct blending of the pyrolysis oils into diesel fuel [35,36], the obtained results confirmed the studies in which further modification of the properties of the pyrolysis oils is assumed [22,23,37].

The presence of the pyrolysis oil from plastics negatively affected the cold-flow properties, and compared to the product of standard processing, there was an increase of 7 °C. This fact was due to the increased content of paraffinic-bound carbon. For these reasons, the possibility of modifying the cold-flow properties using the additive was verified. The additivation favourably affected the CFPP value of the measured samples. The pure SRGO could be used during the summer to winter transition period (or winter to summer) with an additive concentration of 200 mg·kg^{−1}. T could also be used in this period, but with a higher concentration of the added additive (400 mg·kg^{−1}). P did not show the required values for the transition period at a concentration of 600 mg·kg^{−1}; therefore, a higher concentration would be required, which raises questions about the feasibility in terms of the production economics. However, the products of T and the SRGO meet the CFPP values for the summer diesel class (0 °C) even without additives. The improved low-temperature properties of the POT can be attributed to the higher levels of the aromatic hydrocarbons, compared to that in waste plastics, in which the hydrocarbon structures are more linear, in the form of n-paraffins [38].

These additives were investigated with the prospect that the use of the existing technologies would reduce the cost of processing the pyrolysis oils. Following the processing of the waste materials into pyrolysis oils, the POP can be used in refineries with standard feedstock for hydrogenating middle distillates and for producing fuels without substantial impacts on the existing technology. The exception is the additivation step, which would have to be optimised for this application. The additives are traditionally tailored to a given matrix and need to be modified for this purpose [39]. This fact is confirmed by the mentioned results, from which it follows that the additive for the standard product worked most effectively. The addition of the POT requires a higher reaction temperature for processing and it could adversely affect the properties of the catalyst in the long-term operation, also taking into account the several times higher content (almost fivefold) of the nitrogenous substances with the inhibitory effect.

The evaluation and comparison of the two catalysts after a short experiment, showed minimal differences and can be considered identical. The catalyst surface homogeneity showed no differences. The chemical composition of the catalyst was analysed with a particular focus on carbon, sulphur and metal levels. Higher differences were found when analysing the active surface of the catalyst before and after processing.

5. Conclusions

- Both pyrolysis oils need to be treated for further refinery applications and can be processed using existing hydrogenation technologies.
- Pyrolysis oil from tyres had a higher effect on the activity of the hydrosulphurisation catalyst. In the long term, higher operating costs as well as faster deactivation of the catalyst is expected.
- The quality of the products depends on the quality of the input raw materials, the product of the co-processing of the pyrolysis oil from the waste plastics showed worse cold-flow properties.

- A comparison with the EN 590 standard shows that the products meet this standard in most values; the others can be further modified.
- The use of additives for the cold-flow properties has shown that the products (diesel) can be used through summer and transition periods.

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Abbreviations

BTX	benzene, toluene, xylene
CFPP	Cold filter plugging point
CO ₂	carbon dioxide
HDS	hydrodesulphurisation
LDPE	low-density polyethylene
NO _x	mono-nitrogen oxides
P	designation of processing of feedstock with pyrolysis oil from plastic
PAH	polycyclic aromatic hydrocarbon
PE	polyethylene
POP	pyrolysis oil from plastic
POT	pyrolysis oil from tyres pyrolysis
PP	polypropylene
PVC	polyvinyl chloride
REB	Russian export blend
SiC	silicon carbide
SRGO	straight run gas oil
T	designation of processing of feedstock with pyrolysis oil from tyres
WABT	weighted average bed temperature

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