



Production of transportation fuels via hydrotreating of scrap tires pyrolysis oil

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ABSTRACT

The hydrotreating of scrap tires pyrolysis oil over commercial Ni-Mo/Al₂O₃ catalyst was researched for the best processing scheme allowing the production of high-quality alternative transportation fuels components of gasoline, jet, diesel, and marine fuel. Despite the initial high content of olefins, aromatics, sulfur, and nitrogen in pyrolysis oil, fuel components obtained by redistillation after the hydrotreating at 360 °C and 10 MPa met the majority of standard fuel specifications. Although the octane number of the naphtha fraction was lower, this fraction can be used as a component of the gasoline pool directly or after the catalytic reforming. Kerosene fraction can be utilized as jet fuel after the additional mild hydrotreatment or blending with hydroprocessed esters and fatty acids (HEFA) to decrease aromatics content. Diesel fraction can be blended with hydrotreated vegetable oils (HVO) to fulfill the density and cetane index specification. The bottom residue can be utilized as a low-sulfur fuel oil component in marine transportation.

1. Introduction

The global tire market reached a volume of 2.268 billion units in 2021, corresponding to 54.5 million tons of tires, and it is expected to grow (2.665 billion units in 2027) [1]. Tires for passenger cars and trucks are commonly made of rubber (41–48 %), carbon black (20–28 %), metal wires (13–27 %), textile (4–10 %), and additives (7–12 %) [2]. The rubber generally consists of butadiene, styrene-butadiene, and natural polyisoprene. The ratio of these components depends on the tire type [3]. Tires are made with respect to the maximal resistance to mechanical stress and weather conditions; therefore, their natural decomposition is estimated to be 80–100 years [4]. The disposal of scrap tires in landfills and stockpiles can result in significant environmental exposure caused by the non-controlled growth of pests, insects, and rats while increasing the fire risk [5]. The processing of scrap tires is, thus, one of the current ecological challenges and perspective sources of carbon-rich material.

There are several ways in which the scrap tires can be processed,

including retreading of the tires (reuse of whole tires), recovery of the material (shredding of the tires and using the material in the form of rubber chips for secondary products [6]), and chemical recycling (thermal processing of the tires like pyrolysis) or energy recovery (gasification, and combustion). According to World Business Council for Sustainable Development, scrap tires in 2017 worldwide were processed in these ways: material recovery – 42 %, energy recovery – 15 %, landfilling and stockpiling – 12 %, and civil engineering and backfilling – 2 %. The remainder (29 % of scrap tires) were collected with an undetermined end use [7].

Pyrolysis represents a technologically feasible, economically acceptable, and ecologically friendly process for scrap tire recycling [8]. There are three main products of pyrolysis of scrap tires: gases, liquid pyrolysis oil, and solids (char and steel). The gas composed of C₁–C₄ hydrocarbons can be used as a fuel gas for industrial processes (e.g., pyrolysis). The char can be used to produce activated carbon or carbon black. The pyrolysis oil, the primary product of the pyrolysis of scrap tires, is consisted of saturated hydrocarbons, olefins, aromatics, sulfur,

Abbreviations: BTEX, Benzene-Toluene-Ethylbenzene-Xylenes; CFPP, Cold Filter Plugging Point; ECA, Emission Control Areas; FID, Flame Ionization Detector; GC, Gas Chromatography; HEFA, Hydrotreated Esters and Fatty Acids; HVO, Hydrotreated Vegetable Oil; LCO, Light Cycle Oil; MCR, Micro Carbon Residue; PONA, Paraffins Olefins Naphthenes Aromatics; PIONA, Paraffins Isoparaffins Olefins Naphthenes Aromatics; SRGO, Straight Run Gas Oil; STPO, Scrap Tires Pyrolysis Oil; TOS, Time On Stream; ULSFO, Ultra-Low Sulfur Fuel Oil; VLSFO, Very-Low Sulfur Fuel Oil; WHSV, Weight Hourly Space Velocity.

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and nitrogen-containing compounds and can be utilized in several ways.

Due to its aromatic nature, scrap tire pyrolysis oil (STPO) is a suitable feedstock for carbon black production [9,10]. For successful and effective carbon nuclei formation, high content of polyaromatic hydrocarbon precursors is necessary. Carbon black is one of the top 50 industrial chemicals globally and is used as an elastomer-reinforcing agent, a conductive filler, a coating and dyeing agent, and an adsorbent for heavy metals removal.

In contrast to the pyrolysis oils derived from biomass [11], the hydrocarbon-based STPO has been studied by many researchers for its direct utilization as a diesel fuel component [12–14]. Nevertheless, the standard quality of diesel fuel and strict exhaust emissions regulations can hardly be met [14,15]. The content of olefins, S and N compounds, and polyaromatics must be significantly decreased before its utilization as a transportation fuel that may contain only traces of these heteroatoms (often less than 10 ppm of sulfur). The STPO is chemically unstable concerning the chemical nature of the process. Additionally, it can be contaminated with various impurities due to the composition of the used raw material. Because of that, STPO upgrading via hydrotreating is a crucial step before its implementation in oil refineries.

Hydrotreating commonly includes the hydrogenation of olefins and aromatics, the removal of sulfur, nitrogen, and oxygen, and demetallization. Generally, the process results in the improvement of color, reduction of density, increase in the H/C ratio, and significant improvement of the thermal and oxidation stability of the STPO [16]. Oil refineries have extensive experience with fractions of similar properties and composition, i.e., from fluid catalytic cracking or processing liquid fractions from steam cracking of hydrocarbons to olefins. For the study of hydrotreating of STPO and evaluation of catalysts activities under different reaction conditions, the continuous flow laboratory unit with the fixed bed of catalyst should be used.

The hydrotreating of the STPO was studied over several catalysts mainly based on Mo, W, Co, and Ni sulfides [17–20] and nickel phosphide [21]. Although reduced Mo, Ni-Mo, and Co-Mo catalysts were also tested [22], their application is disputable due to the high sulfur content in the STPO. These catalysts used supports based on alumina, silica, activated carbon, and zeolites. The catalysts used for the hydrotreating must be resistant to the high concentrations of sulfur and nitrogen compounds present in the STPO. Presulfided Ni-Mo, Co-Mo, and Ni-W with alumina-based support are, therefore, the common types of catalysts used for this purpose.

On the other hand, several publications have shown that common reaction conditions used for the hydrotreating of middle distillates in refineries may not be effective enough for sufficient sulfur and nitrogen removal and olefins hydrogenation in the STPO [17,19,22]. For example, the sulfur content and bromine number were reduced insufficiently for clean fuels, only by about 91 and 84 %, respectively, when STPO was hydrotreated over Ni-Mo catalyst at 380 °C and pressure 5 MPa [17,19]. Although the reduction of sulfur content by 91 % may sound promising, with respect to the usual sulfur content of STPO (ca. 1 wt%) and limit for sulfur in final products (fuels), at least 99.9 % desulfurization is needed. So far, the most successful desulfurization was published in 2022 by Zhang et al. [23]. The authors tested reduced Ni-Mo catalyst and reached up to 99.9 % sulfur removal when conditions of 375 °C and 4 MPa were tested. However, the authors focused on catalysis itself, and no other information about product properties and quality metrics of fuels were presented.

Problematic sulfur removal is caused by the high content of olefins in STPO, which are hydrogenated preferentially, and a high content of polyaromatic hydrocarbons, which are hydrogenated to monoaromatics. Previous publications have shown that the sulfur in the STPO is present mainly in benzothiazole, benzothiophenes, dibenzothiophenes, and benzonaphthothiophene [20,24,25], which only confirms difficulties connected with deep desulfurization. Sulfur removal is thus one of the main tasks that must be completed when ultra-low sulfur fuels are produced from STPO. Except for hydrotreating, the total sulfur

content in the pyrolysis oil can be reduced by carrying the pyrolysis in a two-stage mode [26] or the presence of acid catalysts [27,28].

Besides the hydrotreating of raw STPO, its co-processing represents an additional perspective way to minimize technological problems in the processing of this recycled feed and the possibility of using existing assets in oil refineries without the need for new investments. The studies focused on co-hydroprocessing STPO with light cycle oil (LCO) from fluid catalytic cracking [29,30], vegetable oil [31], or waste engine oil [32] are available.

As clear from the research of the literature and two latest reviews dedicated to the processing of scrap tires [33,34], there are hundreds of papers focusing on the pyrolysis of scrap tires, describing yields, composition, and direct use of pyrolysis products. However, much less attention is put on the hydrotreating of the STPO as the crucial downstream upgrading step. Any previously mentioned works aiming at STPO hydrotreating did not produce the fuels fulfilling the required standard specification. To the best of our knowledge, in this study, we are thus presenting the first successful effort in producing alternative transportation fuels (gasoline, jet, and diesel fuel) from STPO. The STPO produced by pilot-scale pyrolysis of scrap tires was hydrotreated over a commercial Ni-Mo/Al₂O₃ sulfidic catalyst at different reaction conditions. A comprehensive characterization of distilled products helped us to validate the reaching of our goal. Using a commercial sulfidic hydrotreating catalyst and fixed-bed flow catalytic unit for reasonable TOS (170 h) with insignificant change in catalyst activity is considered a premise for the direct transfer of the obtained results to the praxis.

2. Experimental

2.1. Materials

The STPO utilized in this study was derived from 500 kg scrap tires using the industrial batch pyrolysis unit from Hedwiga Group (Czech Republic). The STPO was stored in tight containers in the dark at a temperature of 5 °C for two months. The basic physico-chemical properties of the STPO are summarized in Table 1.

The yields and basic properties of fractions distilled from the STPO, with a distillation range typical of oil refineries, are specified in Table 2.

2.2. Hydrotreating

The STPO was hydrotreated over a commercial hydrotreating Ni-Mo/γ-Al₂O₃ catalyst in a lab scale fixed-bed catalytic unit (CACTU Solutions, Prague, Czech Republic, www.cactu.eu) with a tube reactor and a co-current flow of the feedstock and hydrogen. The internal diameter and the total length of the reactor were 23 and 490 mm, respectively. The catalyst was crushed, sieved, and 32 g of the fraction 0.25–0.42 mm

Table 1
Basic physico-chemical properties of STPO.

Property	Value	Method used
Appearance	dark brown liquid	–
Density at 15 °C (kg·m ⁻³)	894.3	EN ISO 12185
Kinematic viscosity at 40 °C (mm ² ·s ⁻¹)	1.33	EN 16896
Elemental composition		
Carbon (wt%)	87.7	ASTM D5291
Hydrogen (wt%)	10.6	
Sulfur (wt%)	0.882	EN ISO 20846
Nitrogen (wt%)	0.820	ASTM D4629
Chlorine (mg·kg ⁻¹)	22.0	EPA 9076
Saturates hydrocarbons content (wt%)	12.2	internal method [35]
Boiling point range (°C)	60–460	ASTM D7169
Iodine value (g I ₂ ·100 g ⁻¹ sample)	97.0	ASTM D5554
Total acid number (mg KOH·g ⁻¹ sample)	0.83	ASTM D664

Table 2
Yields and basic properties of fractions distilled from STPO.

Fraction	Yield (wt%)	Sulfur (mg·kg ⁻¹)	Nitrogen (mg·kg ⁻¹)	Iodine value (g I ₂ ·100 g ⁻¹)	Total acid number (mg KOH·g ⁻¹)	Aromatics content (wt%)
up to C ₄	0.5	–	–	–	–	0.0
C ₄ –150 °C	27.0	6100	3500	106.0	0.0	43.0
150 – 250 °C	38.5	9294	9433	91.3	0.23	48.6
250 – 360 °C	22.0	9944	8800	63.9	3.13	78.8
above 360 °C	12.0	11,718	14,061	59.8	2.55	90.8

was diluted with silicon carbide (fraction 0.09–0.106 mm) in the volume ratio 1:1. The diluted catalyst was placed in the middle section of the reactor. In contrast, the upper preheating part was filled with glass beads with a diameter of 2.0 mm. The thermo probe (outer diameter 4 mm) with six thermocouples was placed in the axis of the reactor for the control of the temperature in the catalyst bed. The average reaction temperature was calculated as the arithmetic average of temperatures measured by these thermocouples. The diagram and photograph of the used catalytic unit are shown in Fig. 1.

The catalyst was dried, activated (sulfided), and stabilized in situ before the hydrotreating of the STPO. The drying was performed at a temperature of 120 °C, a pressure of 0.5 MPa, and a flow rate of hydrogen 30 dm³·h⁻¹ for 3 h. The catalyst was activated with the mixture of straight run gas oil (SRGO) containing 0.23 wt% of sulfur and 3.0 wt% of dimethyldisulfide at a weight hourly space velocity (WHSV) 1 h⁻¹, pressure 4 MPa, and hydrogen to feedstock ratio of 230 m³·m⁻³. The temperature was increased from 150 to 345 °C at a heating rate of 20 °C·h⁻¹ and held for 6 h at the final temperature. After the activation, the catalyst was stabilized with SRGO at constant conditions: temperature of 290 °C, pressure of 4 MPa, WHSV of 1 h⁻¹ and hydrogen to feedstock ratio of 230 m³·m⁻³ for 48 h.

The STPO was hydrotreated at WHSV of 1 h⁻¹, hydrogen to feedstock ratio of 400 m³·m⁻³, at the temperature range of 210–360 °C (tested from the lowest to the highest reaction temperature, as suggested by the catalyst manufacturer), and pressures of 6 and 10 MPa. For each reaction temperature, the liquid and gaseous product were taken, and the flow rate of off-gas was measured by a membrane volumetric gas flow meter. The liquid and gaseous products were separated in a high-pressure separator. Around 500 g of the liquid product was collected into the glass bottle, and part of the gaseous product was sampled into a Tedlar sampling bag for analysis. For the precise measuring of sulfur content in the primary liquid products of the hydrotreating, an extra 50 g sample was taken directly into the stirred 100 ml flask containing a water solution of sodium hydroxide to remove dissolved hydrogen

sulfide formed during the hydrotreating. Experiments at both reaction pressures were started with a freshly activated catalyst to compare the effect of catalyst deactivation. The testing of one reaction temperature took 24 h and consisted of temperature setup (2 h), reactor and separator flushing (6 h), and liquid product sampling (16 h). Each experiment (at 6 and 10 MPa) took 170 h of TOS (counted for feeding of STPO only). After completing the product sampling at 360 °C, the conditions 210 °C/6 MPa and 240 °C/10 MPa were tested again to check catalyst activity.

2.3. Products analysis

The gaseous products were analyzed via Agilent 6890 N gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) with a flame ionization detector equipped with an Agilent J&W CP CARBOBOND capillary column (50 m × 0.53 mm × 50 µm). The detailed conditions of the analysis were described in our previous work [36].

The STPO and the primary liquid products of its hydrotreating were fractionated into the naphtha (up to 150 °C), kerosene fraction (150–250 °C), atmospheric gas oil (250–360 °C), and bottom residue (above 360 °C) using automatic distillation apparatus Fischer with Spaltrohr column.

The density and kinematic viscosity were measured by SVM 3000 device (Anton Paar, Graz, Austria), and the iodine value was measured according to the ASTM D5554. The total acid number was measured according to ASTM D664 utilizing ten times diluted titrant 0.01 M KOH. The total sulfur and nitrogen contents were determined according to the ASTM D5453 and ASTM D4629 procedures, respectively, on a Trace Elemental Instruments Xplorer-NS (Delft, The Netherlands). The cold filter plugging point (CFPP) was measured according to the ASTM D6371 standard on Callisto 100 (Anton Paar, Graz, Austria).

The hydrocarbon composition of the naphtha fractions (PIONA analysis) was determined using GC/FID analysis equipped with a PONA column (50 m × 0.2 mm × 50 µm). The octane number of naphtha fractions was estimated from the PIONA results based on the additive

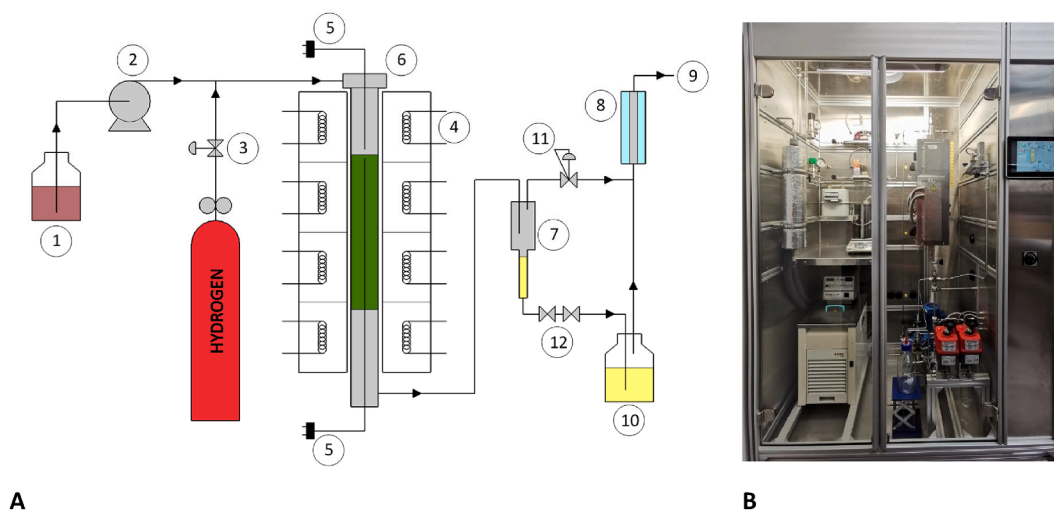


Fig. 1. Diagram (A) and photograph (B) of used catalytic unit, 1-feedstock vessel, 2-high pressure pump, 3-hydrogen mass flow controller, 4-four heating zone furnace, 5-thermowell, 6-fixed bed reactor, 7-high pressure gas/liquid separator, 8-cooler, 9-off-gas outlet, 10-liquid product vessel, 11-pressure controller, 12-drain valves.

volumetric contribution of each hydrocarbon (abundance in volume percentages) and an internal database of octane numbers of respective compounds.

The saturated hydrocarbons in the middle distillates (150–250 and 150–360 °C) were separated using preparative liquid column chromatography described in previous work [35] while the laboratory temperature was applied in this case. The mass content of saturates in the eluate was determined by GC/FID analysis over the Ultra-1 column (20 m × 0.32 mm × 0.52 μm). The conditions of GC/FID analysis were the following: injected amount of 1 μl; split ratio of 1:10; injector temperature of 250 °C; constant pressure of nitrogen of 25 kPa; temperature program: 40 °C for 5 min, 5 °C·min⁻¹ to 300 °C with a hold time of 10 min. The measurement was carried out in agreement with ASTM D2786. The content of aromatics and non-hydrocarbons in middle distillates was determined by the GC × GC-FID technique. LECO's QuadJet SD was composed of an Agilent 7890B GC (Agilent, Santa Clara, CA) with a non-moving quad-jet dual-stage modulator (LECO Corporation, St. Joseph, MI), liquid nitrogen cooling, UHP He carrier gas, 30 m mid-polar primary column DB-17 ms (Agilent, Santa Clara, CA), and 0.8 m nonpolar secondary column DB-1 ms (Agilent, Santa Clara, CA). The olefin content was calculated from the content of saturates (column chromatography) and the content of aromatics and non-hydrocarbons (GC × GC-FID) as a difference up to 100 wt%. The cetane index of diesel fractions (distillation range of 150–360 °C) was calculated from the density and simulated distillation (SIMDIST) results according to ASTM D4737 where TRACE GC Ultra-Thermo Fisher Scientific (Waltham, MA, USA) equipped with a CP-SimDist column (10 m × 0.53 mm × 17 μm) was used for the SIMDIST measurements.

Bottom residues were separated into saturates and unsaturates using the same preparative liquid column chromatography method mentioned above [35]. The micro carbon residue (MCR) of bottom residues was measured according to ASTM D4530 using a Normalab Analysis NMC 420 device.

The distribution of *n*-alkanes, isoalkanes, and cycloalkanes groups within the separated fractions of saturates was obtained using GC/MS technique (Trace Ultra GC and DSQ II mass spectrometer; Thermo Fisher Scientific). DB-5 ms column (30 m × 0.25 mm × 0.25 μm) was used for the analysis. The measurement was carried out in agreement with ASTM D2786.

2.4. Hydrogen consumption

The hydrogen consumption during the hydrotreating was calculated from the hydrogen content in off-gas (without unconsumed hydrogen) and primary liquid product and their flow rates for each combination of pressure and temperature. The hydrogen content in off-gas was calculated from GC-FID results as a difference up to 100 wt% after subtraction of hydrocarbon content. The hydrogen content in primary liquid products was measured by elemental analysis according to ASTM D5291. The complete procedure of hydrogen consumption calculation is described in the [Supplementary Information](#) section.

2.5. Used catalyst characterization

After each hydrotreating experiment, the used catalyst was flushed with toluene and *n*-heptane, dried, and sampled by layers to describe the coke formation in the catalyst bed. The carbon content in catalyst samples was determined by elemental analysis using Elementar vario EL Cube (Elementar, Langensfeld, Germany).

3. Results and discussion

3.1. Composition of primary gaseous and liquid products from hydrotreating of STPO

The appearance of hydrotreated liquid products gradually changed

from dark brown to colorless as the temperature of hydrotreating increased (Fig. 2). The appearance of the liquid products was not dependent on the reaction pressure.

A small formation of gaseous products up to C₄ commonly accompanies the hydrotreating of hydrocarbons. In the case of STPO hydrotreating, the yield of gases up to C₄ increased with the increasing temperature. The maximum yield was ~1.3 wt% when the highest reaction temperature of 360 °C and pressure of 10 MPa were applied (Fig. 3). The dominant component of the gaseous products was isobutane along all reaction conditions. Furthermore, all gaseous products contained methane, ethane, propane, and *n*-butane. Butenes were found only at low reaction temperatures of 210 and 240 °C.

The density decreased with the increasing reaction temperature, which proves the aromatics were hydrogenated at an increasing rate (Fig. 4A). It is evident that the hydrogenation activity of the used Ni-Mo catalyst was enhanced at the highest reaction temperatures (330 and 360 °C) when higher pressure (10 MPa) was applied. Based on the iodine values, it was shown that a reaction temperature of at least 330 °C was necessary for the complete hydrogenation of olefins (Fig. 4B). At the lower reaction temperatures up to 300 °C, the hydrodesulfurization was easier when compared to hydrodenitrogenation (Fig. 4C and 4D). The desulfurization and denitrogenation activity of the used catalyst depended on the reaction pressure, especially at temperatures above 300 °C. The sulfur and nitrogen contents were successfully reduced under 10 mg·kg⁻¹ at 360 °C and 10 MPa. In contrast to our results, Debek and Walendziewsky [17] and Hita et al. [19], studying STPO with comparable sulfur content, reported three orders of magnitude higher sulfur content (1000 ppm) for STPO hydrotreated over sulfided Ni-Mo catalyst at 360 °C, 5 MPa, and 375 °C, 6.5 MPa, respectively. Both commented studies applied higher space velocity for hydrotreating, which could be the explanation for the poorer desulfurization.

The yields of the primary liquid products varied between 98.7 and 99.5 wt%. The mass increase in relation to reaction temperature was caused by the hydrogen consumed for the hydrogenation of olefins and aromatics. On the other hand, the mass decrease was caused by the formation of gaseous hydrocarbons (Fig. 3) and by the elimination of sulfur and nitrogen from the STPO in the form of H₂S and NH₃ (Fig. 4C and 4D). Finally, the yield of the primary liquid product decreased from 99.5 to 98.7 wt% with increasing temperature at 6 MPa and from 99.5 to 99.0 wt% at 10 MPa.

The yield of each fraction (gases up to *n*-butane), naphtha (C₅–150 °C), kerosene (150–250 °C), atmospheric gas oil (250–360 °C), and bottom residue (above 360 °C) was not significantly affected by the hydrotreating (Fig. 5). PIONA analysis showed that a part of the gaseous product (up to C₄) was contained in the naphtha fraction and vice versa. The yield of gases up to C₄ was, therefore, calculated as a sum of the yield of hydrocarbons in the boiling point range of methane to *n*-butane via the PIONA analysis of off-gas and relevant naphtha fraction (Equation S1). Similarly, the yield of naphtha was calculated as a sum of the yield of hydrocarbons above *n*-butane in relevant off-gas obtained from PIONA and the yield of distilled naphtha without hydrocarbons up to C₄ (Equation S1). Only at the reaction temperatures above 270 °C, the yield of naphtha slightly increased (from 27 to 33 wt%) at the expense of atmospheric gas oil and bottom residue. The yield of kerosene varied between 38.5 and 41.7 wt%, and its dependence on the reaction temperature was not observed. The yield of atmospheric gas oil and bottom residue decreased from 22.0 and 12.0 wt% to 18.0 and 6.2 wt%, respectively, after the hydrotreating at 360 °C and 10 MPa.

3.2. Composition and properties of naphtha fraction (C₅–150 °C)

The naphtha fraction distilled from the STPO contained 26.5 wt% olefins and 43.2 wt% aromatics. The remainder was formed by *n*-alkanes (2.7 wt%); isoalkanes (11.7 wt%), cycloalkanes (12.7 wt%), oxygen-compounds (1.2 wt%), sulfur-compounds (1.4 wt%) and nitrogen-compounds (0.5 wt%). Mainly C₇ aliphatic (4.9 wt%) and cycloalkanic

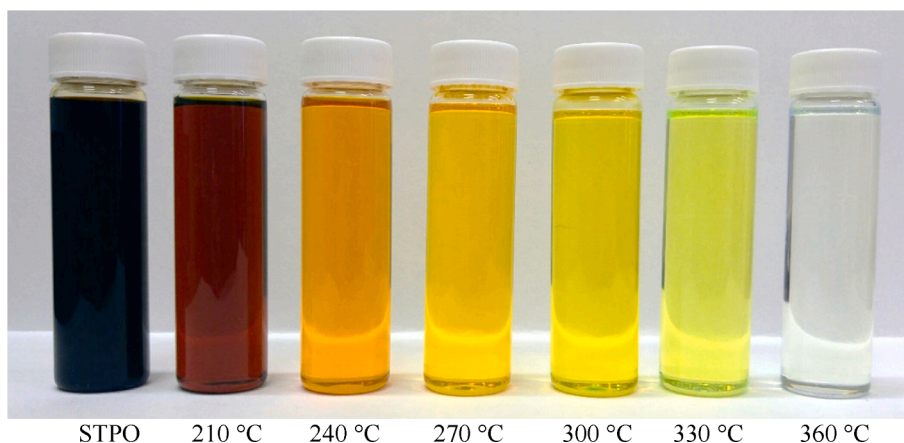


Fig. 2. Appearance of the STPO (on the left) and the hydrotreated liquid products obtained at various temperatures and 10 MPa pressure.

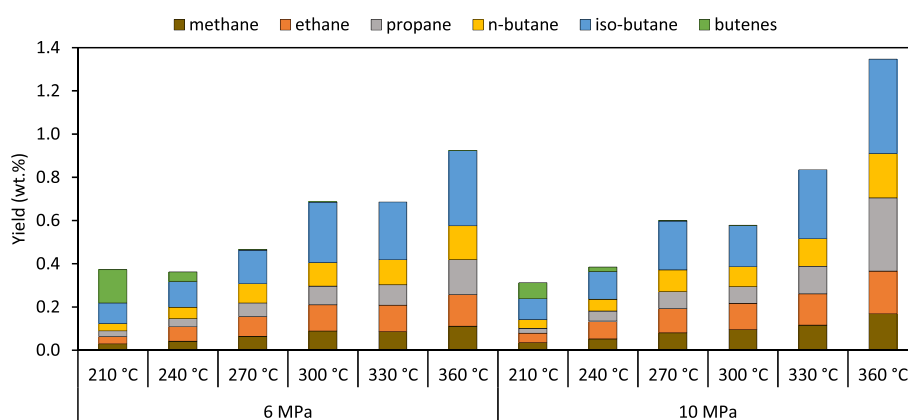


Fig. 3. Yield of gaseous compounds from the hydrotreating of the STPO (related to the feedstock).

olefins (6.0 wt%) were present in the naphtha from STPO. The changes in the group-type composition of hydrotreated naphtha are summarized in Fig. 6. While the olefins were transformed into *n*-alkanes, isoalkanes, and cycloalkanes, the aromatics were partially hydrogenated to cycloalkanes. After the hydrotreating, the naphtha fraction still contained a larger portion of aromatics (at least 33.2 wt%). When this value is compared with the aromatics content in the naphtha from the STPO (44.2 wt%), 24.9 % dearomatization of the naphtha fraction was achieved during the hydrotreating at the most severe tested reaction condition (360 °C and 10 MPa) utilized in this study.

The density of the naphthas (EN 228 upper limit of 775 kg·m⁻³) decreased from 807 kg·m⁻³ for the fraction obtained from the raw STPO down to 775 kg·m⁻³ for the fraction obtained at 360 °C and 10 MPa (Fig. 7A). Only a negligible effect of the reaction pressure on the naphtha density was observed.

The naphtha distilled from the STPO contained 6100 and 3500 ppm of sulfur and nitrogen, respectively (Fig. 7B and 7C). The higher pressure of the hydrotreating only slightly enhanced the desulfurization and denitrogenation of the naphthas. The naphthas obtained at the temperature ≥ 300 °C at 10 MPa fulfilled the requirement for gasoline sulfur content. The total acid number of the naphtha fractions was very low (<0.05 mg KOH·g⁻¹), even for naphtha from the untreated STPO.

To reduce the initial aromatics content of 43 vol% determined in the STPO naphtha closer to the EN 228 standard upper limit of 35 vol%, the hydrotreating temperature of at least 330 °C and reaction pressure 10 MPa should be applied (Fig. 7D). Additionally, at the lower reaction pressure (6 MPa), a temperature around 345 °C should be used. On the other hand, reducing aromatics content may not be crucial if the

naphtha is considered a gasoline component blended with other non-aromatic components (isomerate, alkylate, oxygenates). The total removal of olefins from naphtha fractions may not be required as olefins increase the octane number. The lowest obtained benzene content of 3.1 vol% was three times higher than the EN 228 standard limit of 1 vol% (Fig. 7E). On the other hand, it can be easily reduced by co-processing on reformate redistillation if available at a refinery.

Despite the relatively high aromatics content, the octane number of any naphtha fraction calculated from PIONA results was not sufficiently close to the target value of 95. In the case of the 360 °C/10 MPa sample, the octane number was even only 79 (Fig. 7F). The low octane number values were caused by the high content of cycloalkanes formed from cycloolefins and aromatics and the insignificant branching of the present isoalkanes.

The hydrotreated naphtha fraction could be used as an alternative component in the gasoline pool. Due to the high content of cycloalkanes and minimal concentration of sulfur (≤ 1 mg·kg⁻¹), which is important for a noble metal-based catalyst, the naphtha fraction obtained at 360 °C and 10 MPa could be a promising feedstock for catalytic reforming. The obtained reformate could be used as a gasoline component or as a valuable source of basic monoaromatics benzene, toluene, ethylbenzene, and xylenes (BTEX) used in the downstream petrochemical industry. BTEX are essential intermediates for producing many chemicals, polymers, detergents, drugs, etc. The content of BTEX in distilled naphtha fractions was in the range of 30.7–44.2 wt% and decreased with increasing reaction temperature (Fig. 8). In contrast, the reaction temperature did not significantly affect the distribution of BTEX.

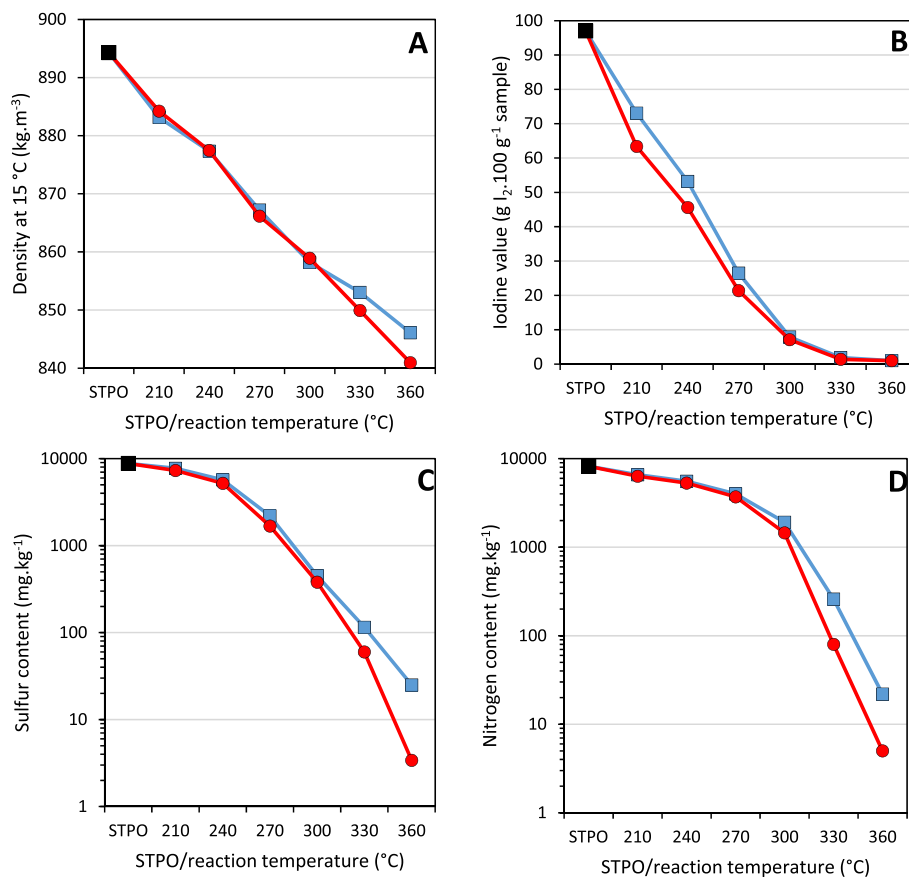


Fig. 4. Density (A), iodine value (B), sulfur content (C), and nitrogen content (D) of STPO and primary liquid hydrotreated products (STPO – black square, 6 MPa – blue squares, 10 MPa - red dots).

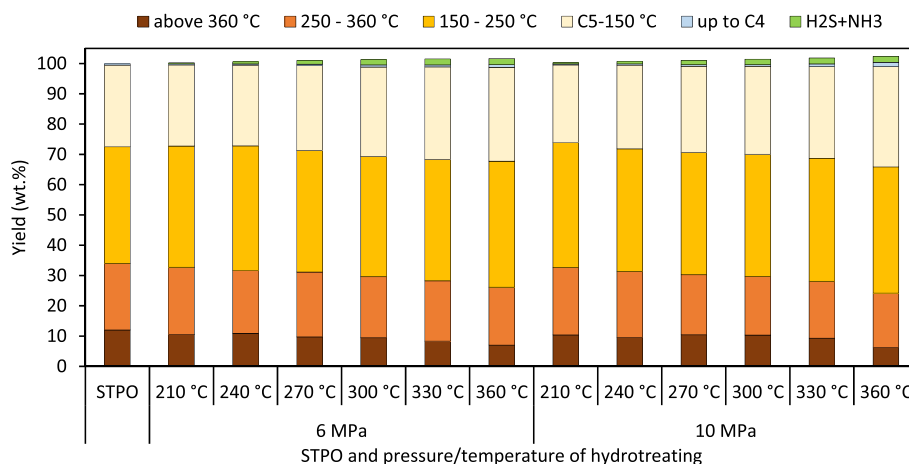


Fig. 5. Yield of H₂S + NH₃, gaseous hydrocarbons, naphtha, middle distillates, and bottom residue from the STPO and products of its hydrotreating.

3.3. Composition and properties of kerosene (150–250 °C)

Kerosene, the major fraction obtained from the STPO contained almost 49 wt% of aromatics and 39 wt% of olefins. The content of the most favorable saturated hydrocarbons was only 7.4 wt%. As evident from Fig. 9, if the STPO was hydrotreated at 6 MPa, only olefins, diaromatics, and non-hydrocarbons were hydrogenated into saturated hydrocarbons and monoaromatics. At 360 °C and 10 MPa, significant hydrogenation of monoaromatics to cycloalkanes was first observed. At this reaction conditions, the content of cycloalkanes increased from the

initial 5.6 to 58.6 wt%, the content of *n*- and isoalkanes increased from 1.8 to 7.6 wt% and, on the other hand, the content of aromatics decreased from 48.6 to 33.5 wt%. which corresponds to 32.1 vol%. The limit for naphthalenes content in JET A-1 (≤ 3 vol%) specified by ASTM D1655 was reached already after the hydrotreatment at 270 °C.

The hydrogenation of unsaturated compounds (olefins and aromatics) and non-hydrocarbons in the STPO resulted in a gradual decrease in the density of kerosene from the initial value of 891 kg·m⁻³ down to 848 kg·m⁻³ when conditions 360 °C and 10 MPa were applied (Fig. 10A). The density limit specified for JET A-1 (775–840 kg·m⁻³)

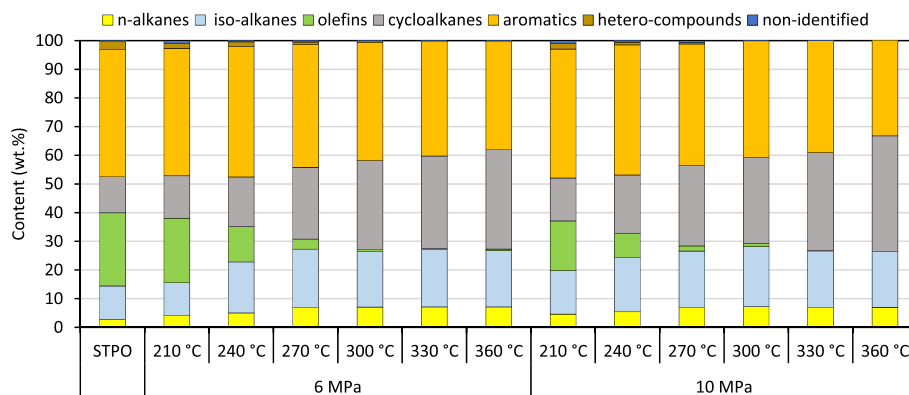


Fig. 6. Group-type composition of naphtha fractions from the STPO and hydrotreated liquid products.

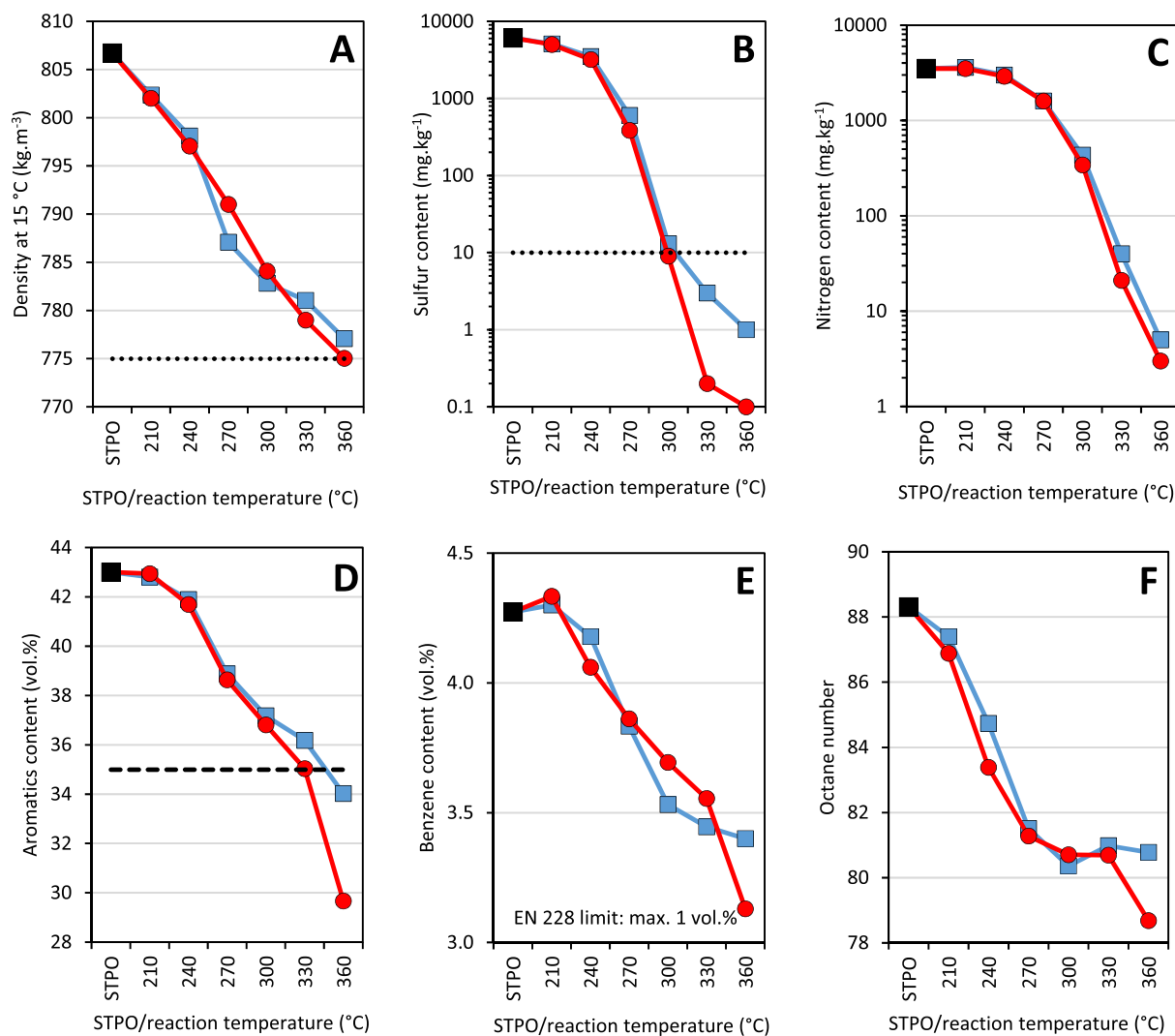


Fig. 7. Basic properties of naphtha fraction from the STPO and hydrotreated products at various temperatures and pressures: density at 15 °C (A); sulfur content (B); nitrogen content (C); total aromatics content (D); benzene content (E) and octane number (F) - (STPO – black square, 6 MPa – blue squares, 10 MPa - red dots, EN 228 limit - dotted line).

was not fulfilled for the studied fraction 150–250 °C; however, by reducing the distillation end, the density limit could be met. The sulfur content decreased from 9300 mg.kg⁻¹ to 2 mg.kg⁻¹ at 360 °C and 10 MPa (Fig. 10B). Since the sulfur content is not strictly limited for JET A-1 (max. 3000 mg.kg⁻¹), the required limit was fulfilled when 270 °C was

applied for the hydrotreating. The nitrogen content decreased from 9400 mg.kg⁻¹ to 6 mg.kg⁻¹ (Fig. 10C). The total acid number decreased from 0.23 to less than 0.05 mg KOH.g⁻¹ sample when temperatures above 210 °C were applied, which is in accordance with the JET-A1 fuel specification limit of 0.1 mg KOH.g⁻¹ sample.

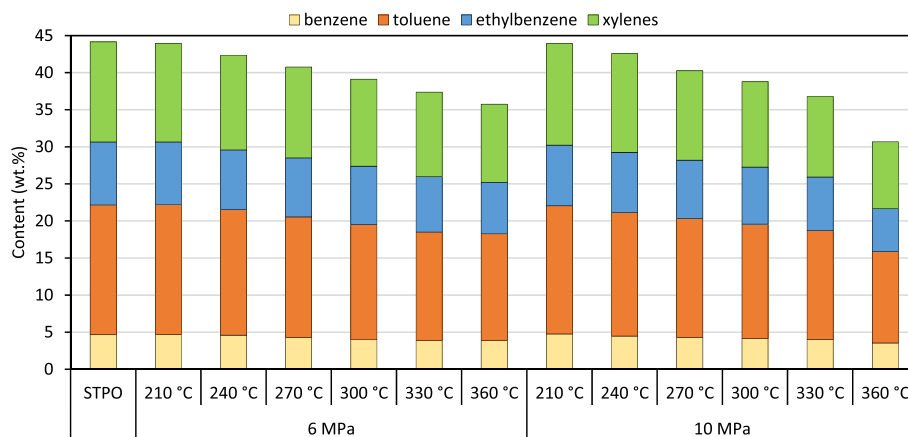


Fig. 8. Content of BTEX in naphthas from the STPO and hydrotreated products.

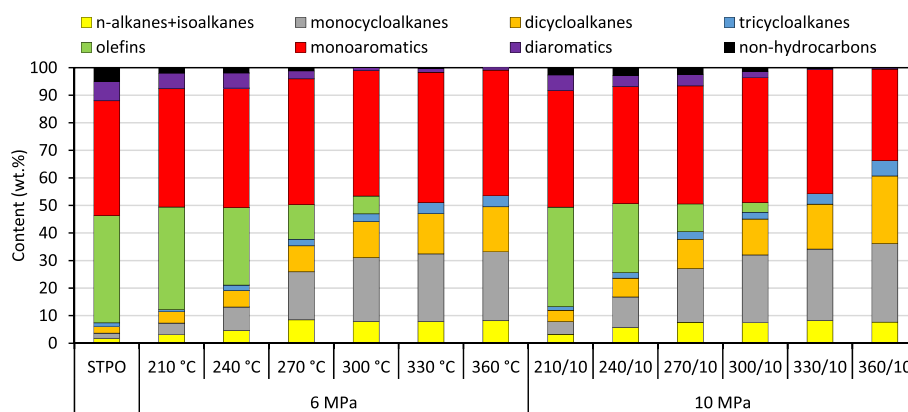


Fig. 9. Group-type composition of kerosenes (150–250 °C) from the STPO and hydrogenated products at various temperatures and pressures.

The smoke point of kerosenes was estimated from the aromatic content according to the equation presented in the work of Kittel et al. [37] (Fig. 10D). The calculated smoke point of around 16 mm for kerosene obtained at 360 °C and 10 MPa (32.1 vol% of aromatics) was slightly below the lower limit of 18 mm for JET-A1 if naphthalenes content is below 3 vol%. On the other hand, if the additional selective hydrotreating of kerosene fraction is applied, further dearomatization would be achieved. According to Kittel et al. [37], even moderate reaction conditions of hydrotreating (320 °C and 6 MPa) should assure the fulfillment of the ASTM D1655 standard specification for aromatics content and accompanying smoke point. Concerning low sulfur content (up to 2 mg·kg⁻¹) in kerosene obtained at 360 °C and 10 MPa, a high-efficient hydrogenation catalyst based on noble metals could be used instead of common sulfidic hydrorefining types. The product of such dearomatization could become a special jet fuel with high volumetric energy due to high content of cycloalkanes.

The alternative to the additional refining step could be the blending of the hydrotreated STPO kerosene obtained at 360 °C and 10 MPa with low-aromatic bio-based aviation fuel, such as hydroprocessed esters and fatty acids (HEFA). The maximum content of aromatics in HEFA is 0.5 wt % according to ASTM D7566. Therefore, ~25 vol% of HEFA should be sufficient to decrease the STPO kerosene aromatic content below the limit of 26.5 vol%. This approach should simultaneously fulfill the specification for density and smoke point. Finally, in the next section, the utilization of kerosene fraction as a component of diesel fuel is evaluated and discussed.

Several works focused on the pyrolysis of scrap tires, and discussed the formation of limonene [38,39]. Limonene is formed by the depolymerization of polyisoprene in natural rubber, followed by

intramolecular cyclization and β -scission [39]. Due to its boiling point of 176 °C, limonene is a part of the kerosene fraction, and its hydrotreating into bio-jet fuel was also studied. [40] The limonene yield is affected by the content of natural rubber in the tire and the type and conditions of the pyrolysis [39]. It can reach even 50 wt% if truck tires are pyrolyzed [41]. Regarding our work, the limonene content in the STPO was only 2.5 wt%. Furthermore, it was easy to hydrogenate limonene and, therefore, only up to 1.5 wt% of limonene was found in the hydrotreated kerosenes obtained at 210 a 240 °C.

3.4. Composition and properties of diesel fraction (150–360 °C)

In this section, the composition and properties of the fraction 150–360 °C, composed of kerosene and atmospheric gas oil blended in the same ratio as the ratio of their distillation yields will be discussed. The results for gas oil fraction are summarized in Tables S3 and S4. Diesel fuel fraction has the potential as an alternative component to diesel fuel. The group-type composition of diesel fractions from the STPO and its hydrotreated products is summarized in Fig. 11.

As evident from Fig. 11, mainly olefins are transformed into cycloalkanes, and polyaromatics are hydrogenated into monoaromatics at 6 MPa. Olefins in the diesel fraction were hydrogenated above 300 °C at both pressures. When the temperature of 360 °C and pressure of 10 MPa were applied, monoaromatics hydrogenation into cycloalkanes (especially di- and tricycloalkanes) exceeded their creation from diaromatics. Detailed GC × GC analysis revealed that almost half of the monoaromatics were present in the form of monocyclo- and dicycloalkane aromatic compounds. The content of polyaromatic hydrocarbons is limited by the EN 590 standard for diesel fuels to max. 8 wt%, and in

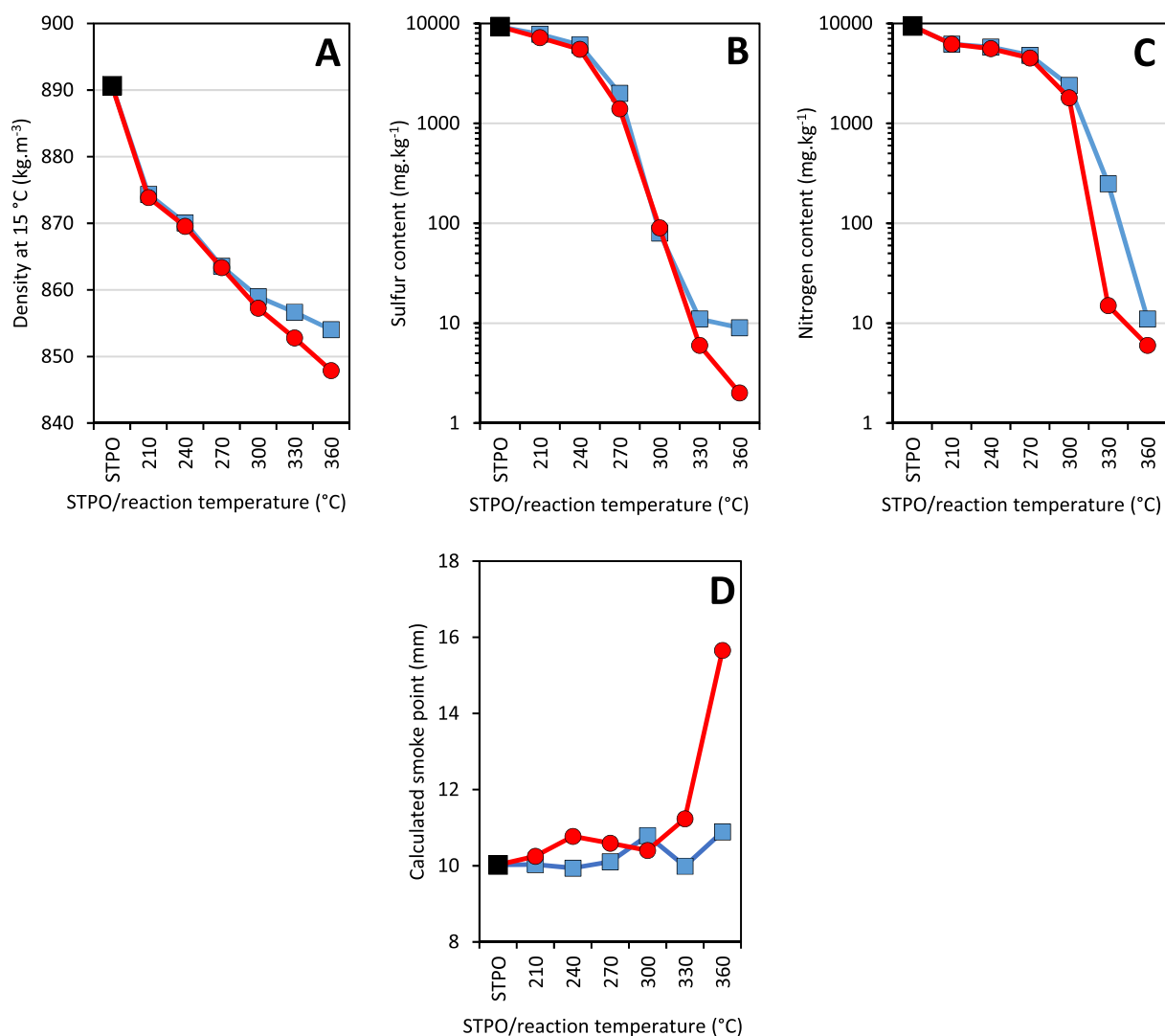


Fig. 10. Basic properties of kerosene fractions from the STPO and hydrogenated products at various temperatures and pressures: density at 15 °C (A); sulfur content (B); nitrogen content (C); calculated smoke point (D) - (STPO – black square, 6 MPa – blue squares, 10 MPa - red dots).

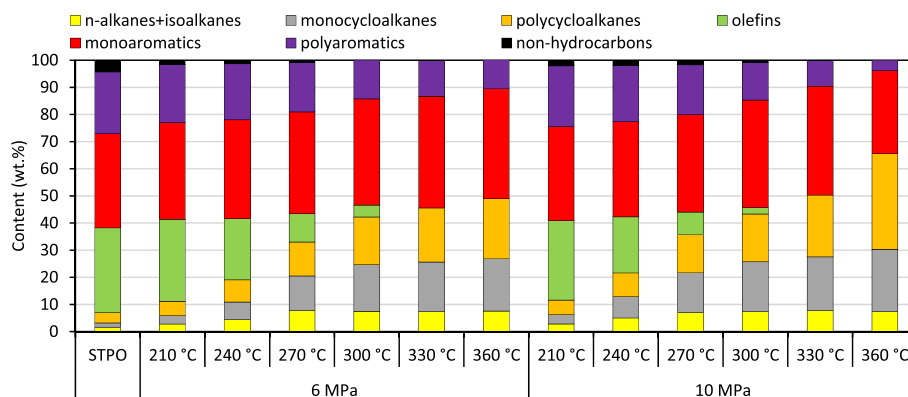


Fig. 11. Group-type composition of diesel fraction (150–360 °C) from the STPO and hydrotreated products at various temperatures and pressures.

our case, it decreased from 22.5 wt% (STPO diesel fraction) to 3.8 wt% (diesel obtained at 360 °C and 10 MPa).

In the following paragraphs, the critical properties of diesel fractions are discussed (Fig. 12). The density of the non-hydrotreated STPO diesel fraction was 913 kg.m⁻³ and dropped to 864 kg.m⁻³ at 360 °C and 10 MPa. This value is, however, still out of the limit specified by the EN 590

standard (820–845 kg.m⁻³) (Fig. 12A). High density values are attributed to the high contents of aromatics and cycloalkanes instead of preferred low-branched isoalkanes. The cetane index (Fig. 12B) ranged from 25.5 for non-hydrotreated STPO diesel fraction to 31.9 for diesel fraction obtained at 360 °C and 10 MPa. The same increase (from 25 to 31) in cetane index for diesel fraction was observed by Hita et al. [19] for

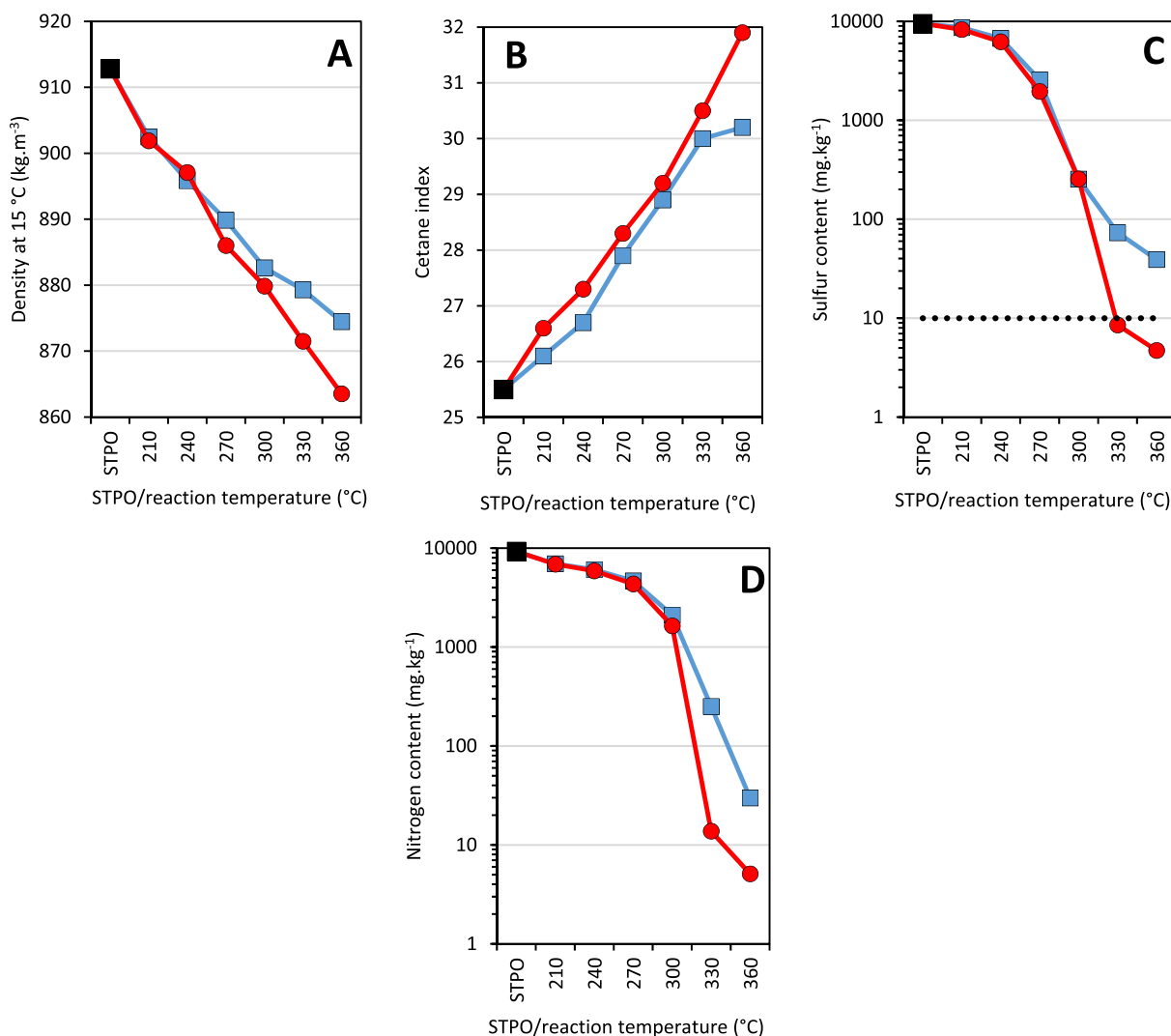


Fig. 12. Basic properties of diesel fractions 150–360 °C distilled from the STPO and the hydrotreated STPO at various reaction temperatures and pressures: density at 15 °C (A); cetane index (B); sulfur content (C); nitrogen content (D)-(STPO - black square, 6 MPa - blue squares, 10 MPa - red dots, EN 590 limit - dotted line).

STPO hydrotreating at 375 °C and 6.5 MPa over Ni-Mo/Al₂O₃ catalyst. The lower limit of cetane index of 46 according to EN 590 was, therefore, not achieved because saturated hydrocarbons (65.8 wt% at 360 °C and 10 MPa) were composed predominantly of cycloalkanes with a lower cetane index than *n*-alkanes and slightly branched isoalkanes.

The sulfur content was the following critical parameter because of the initial sulfur content (9480 mg.kg⁻¹) in the diesel fraction from the STPO. Only diesel fractions obtained at 330 and 360 °C and 10 MPa can fulfill the EN 590 limit of 10 mg.kg⁻¹ (Fig. 12C). During the hydrotreating, the nitrogen content decreased from the initial value of 9250 mg.kg⁻¹ to 5 mg.kg⁻¹ at the highest reaction temperature and pressure (Fig. 12D). As evident from Fig. 12, the pressure increase played an essential role in reaching deep desulfurization and denitrogenation, as well as density reduction and cetane index improvement.

To conclude, diesel fractions obtained at 330 and 360 °C and 10 MPa have the potential to become an alternative component of diesel fuel. Nevertheless, due to their high density and high content of aromatics, their cetane indexes are still much lower (31 and 32) than the EN 590 limit (min. 46). An additional hydrotreating step might have only a little effect on the cetane index because it would increase the content of cycloalkanes which already is relatively high. Except for blending with standard fossil diesel fuel, the obtained diesel fraction could be blended with a fraction containing mainly *n*- and isoalkanes, having low density

and high cetane index. To verify this hypothesis, a commercial hydro-treated vegetable oil (HVO) from Neste Company was used. The basic parameters of used HVO are listed in Table S1. HVO was added into two diesel fractions (330/10 and 360/10) in concentrations of 25, 30, and 35 wt%. Values of critical parameters from the EN 590 standard are summarized in Fig. 13. Adding 25 and 30 wt% of HVO to the diesel fraction 360/10 and 330/10, respectively, was sufficient to reach the specified density and kinematic viscosity limits. On the other hand, adding at least 35 wt% of HVO into both diesel fractions was necessary to increase the cetane index above the minimum limit of 46.

CFPP describing the low-temperature behavior of diesel fuel was also measured. The diesel fractions from STPO hydrotreated at temperatures 330 and 360 °C and pressure 10 MPa had CFPP -38 and -39 °C, respectively. By adding HVO in the concentration of 25–35 wt%, the CFPP slightly decreased to the values of -41 and -42 °C, which is far below the EN 590 limit (max. -20 °C) specified for diesel class F (winter) for moderate climate regions. These values would even fulfill the CFPP requirement for arctic diesel class 0, 1, 2, and even 3 (upper limit of CFPP -38 °C).

In any case, hydrotreated diesel fractions obtained at 330 and 360 °C and 10 MPa can be used as a component for diesel fuel blending, having excellent low-temperature properties. The higher density and lower cetane index just must be considered.

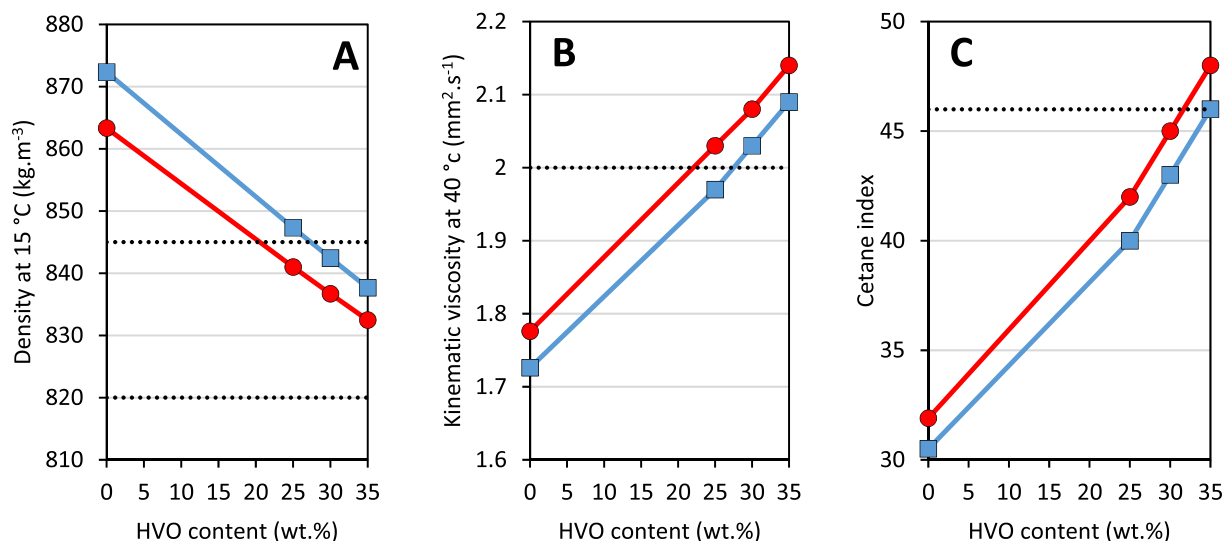


Fig. 13. Basic properties of diesel fuel mixed from hydrotreated STPO diesel fraction and HVO: density at 15 °C (A); kinematic viscosity at 40 °C (B); cetane index (C) - (330 °C/10 MPa – blue squares, 360 °C/10 MPa - red dots, EN 590 limit - dotted line).

3.5. Composition and properties of bottom residue (above 360 °C)

The bottom residue obtained from the STPO contained almost 1.2 wt% of sulfur, 1.4 wt% of nitrogen, 9.3 wt% of saturated compounds, and more than 90 wt% of unsaturated compounds (olefins and aromatics), and hetero compounds. The content of Conradson's carbon residue was

5.8 wt% (Fig. 14B). After the hydrotreating, the properties of the bottom residue were improved significantly. At the highest reaction temperature and pressure (360 °C and 10 MPa), the bottom residue contained 66.7 wt% of saturates, 9 and 16 mg.kg⁻¹ of sulfur and nitrogen (Fig. 14A, C and D), respectively, and undetectable content of carbon residue was reached.

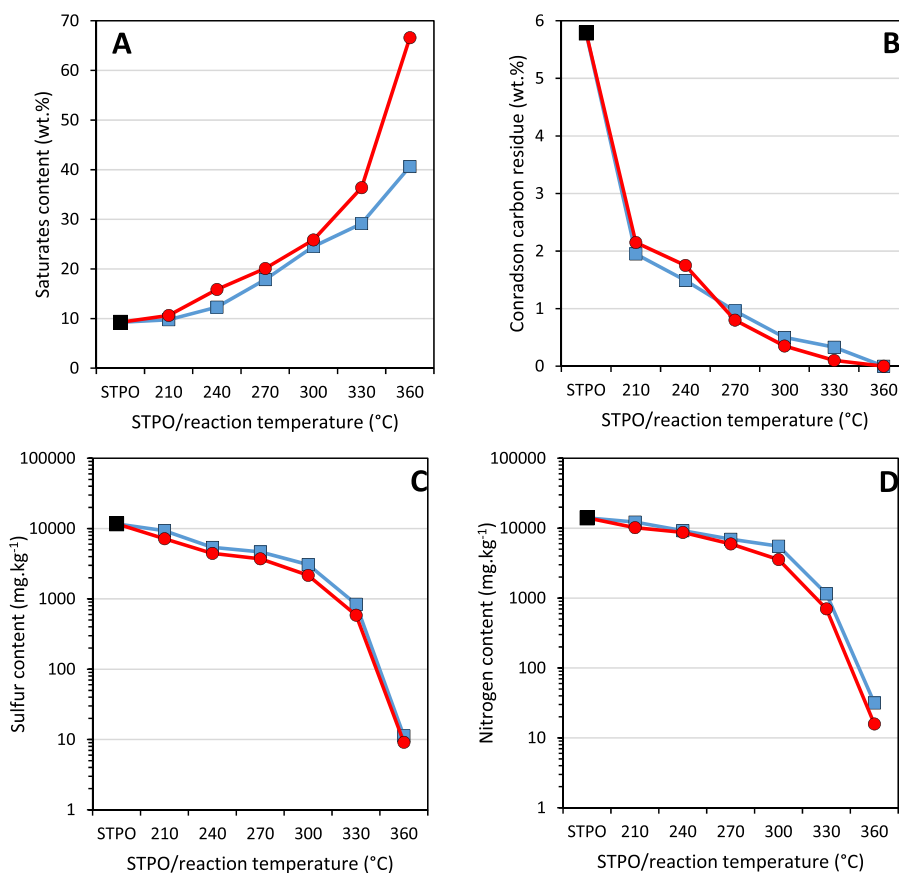


Fig. 14. Basic properties of bottom residues distilled from the STPO and the hydrotreated STPO at various temperatures and pressures: saturates content (A), Conradson carbon residue (B), sulfur content (C), and nitrogen content (D) (STPO – black square, 6 MPa – blue squares, 10 MPa - red dots).

Such a type of upgraded bottom residue can be, for example, utilized as an alternative component of bunker-type very-low sulfur fuel oil (VLSFO) used in marine transportation with a sulfur limit of 0.5 wt%. Due to the sulfur content of $9 \text{ mg}\cdot\text{kg}^{-1}$, it can be utilized in ultra-low sulfur fuel oil (ULSFO) required in emission control areas (ECA) around coasts. From January 2015, fuels with up to 0.1 wt% of sulfur are required in these ECA zones.

The hydrotreated bottom residue can also be hydrocracked for the additional production of high-quality transportation fuels. Due to the low yield of this hydrotreated bottom residue $\sim 6 \text{ wt}\%$ (Fig. 5), its co-processing with a common residual feedstock can be expected.

3.6. Hydrogen consumption

Hydrotreating is a process requiring a source of expensive hydrogen, and its consumption is, therefore, an important parameter. It is necessary to realize that the aim of hydrotreating is not the total saturation of all double bonds. Generally, the compromise of hydrogen consumption and the composition of all obtained distillates to their following utilization is searched. In this section, the hydrogen consumption for hydrogenation of olefins, hydrogenation of aromatics, hydrodesulfurization, and hydrodenitrogenation are compared. The hydrogen consumption was only calculated for the sulfur and nitrogen atoms elimination (and H_2S and NH_3 formation) via hydrodesulfurization and hydrodenitrogenation.

When the STPO was hydrotreated, the total hydrogen consumption grew with the increasing reaction temperature and pressure (Fig. 15). To describe the dependence of total hydrogen consumption on the reaction temperature, the linear regression in the temperature range of $210\text{--}360 \text{ }^\circ\text{C}$ can be successfully applied. The maximum hydrogen consumption for the hydrotreating (at $360 \text{ }^\circ\text{C}$ and 10 MPa) was $23.6 \text{ g H}_2\cdot\text{kg}^{-1}$ STPO, which is about $\sim 7 \text{ g H}_2\cdot\text{kg}^{-1}$ STPO more when compared to the hydrotreating at the same temperature but lower pressure of 6 MPa. This extra hydrogen was consumed for the hydrogenation of aromatics, which improved the properties of the middle distillates and bottom residue.

As evident from the results, most hydrogen was consumed for the hydrogenation of double bonds in olefins, especially at temperatures up to $300 \text{ }^\circ\text{C}$. At a temperature of $240 \text{ }^\circ\text{C}$ and above, hydrogen was partially consumed for the hydrogenation of aromatics. The low consumption of hydrogen for the removal of sulfur and nitrogen (up to $2.4 \text{ g H}_2\cdot\text{kg}^{-1}$ STPO) was given by the relatively low concentration of these heteroatoms in pyrolysis oil when compared to olefins and aromatics. The higher consumption of hydrogen in the case of denitrogenation in comparison with desulfurization despite comparable starting concentration in the STPO is given by a higher relative atomic mass of sulfur (32.07) when compared to nitrogen (14.01). Additionally, the

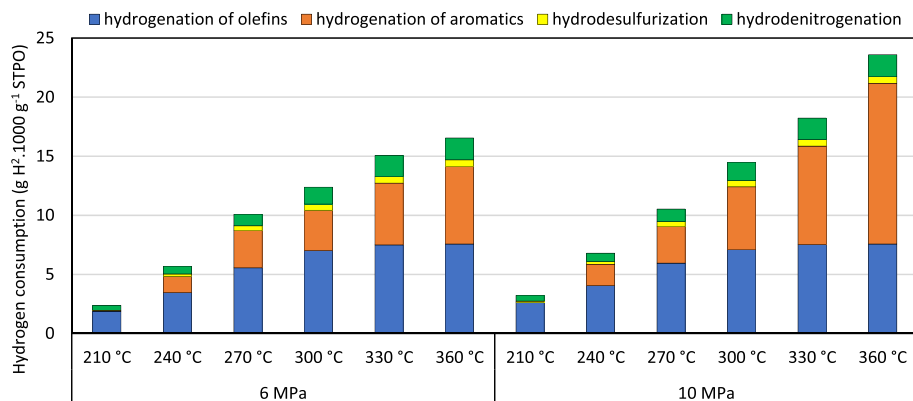


Fig. 15. Total hydrogen consumption in relation to the reaction temperature and pressure for major hydrogenation reactions during the hydrotreating of the STPO.

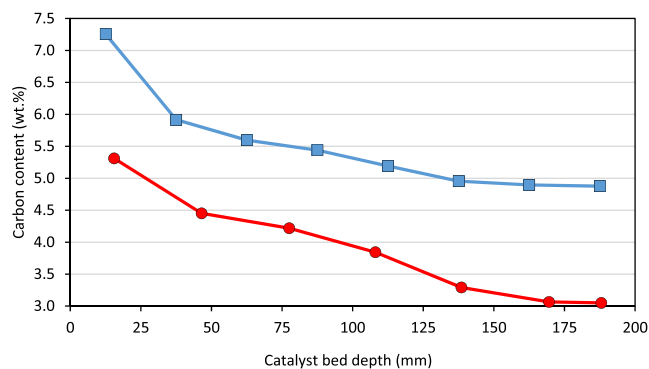


Fig. 16. Carbon content in catalyst layers after STPO hydrotreating - (6 MPa - blue squares, 10 MPa - red dots).

transformation of one nitrogen atom to NH_3 consumes 1.5 times more hydrogen than the conversion of one sulfur atom to H_2S .

3.7. Catalyst deactivation

The deactivation of the catalyst after STPO hydrotreating was evaluated based on carbon content in used catalyst layers and the comparison of selected basic properties (density and bromine number) of check liquid sample collected at the end of the experiment with the primary liquid sample collected at the beginning of the experiment. The temperatures of 210 and $240 \text{ }^\circ\text{C}$ were chosen as check temperatures for 6 and 10 MPa experiments, respectively. As evident from catalyst characterization after the experiment (Fig. 16), when STPO was hydrotreated at higher pressure 10 MPa, less intense coke formation on the catalyst was observed. The content of carbon in the upper and bottom layers of the catalyst bed decreased by about 28 and 37 rel.%, respectively, when pressure 10 MPa was applied and compared to 6 MPa. Besides, the carbon content in the 10 MPa upper layer (5.31 wt%) is close to the carbon content in the 6 MPa bottom layer (4.88 wt%).

Only ca. 0.5 wt% of nitrogen was adsorbed on the catalyst after 170 h of TOS (Fig. S1). The amount of nitrogen decreased with the catalyst bed depth, and as well as in the case of carbon, less nitrogen was adsorbed on the catalyst at higher pressure (10 MPa). No sulfur leaching from the catalyst was observed (Fig. S1). Based on the results of check samples (Table S2), it was shown that during both 170 h hydrotreating experiments, the catalyst did not lose its activity. Slightly better properties of 10 MPa check sample can be attributed to the hydrotreating at a higher temperature $241 \text{ }^\circ\text{C}$ instead of $240 \text{ }^\circ\text{C}$.

4. Conclusion

Scrap tires pyrolysis oil (STPO) was hydrotreated over commercial sulfidic hydrorefining Ni–Mo/γ-Al₂O₃ catalyst at reaction temperatures of 210–360 °C and reaction pressures of 6 and 10 MPa. Significant changes in the chemical composition of the STPO were achieved, in particular complete hydrogenation of olefins, reduction of aromatics (mostly polyaromatics), deep desulfurization, and denitrogenation. The changes in the chemical composition resulted in significant improvements in the properties of the hydrotreated fuel fractions in terms of blending into transportation fuels.

The naphtha fraction obtained from the STPO hydrotreated at a temperature of 360 °C contained less than 1 mg·kg⁻¹ of sulfur. It could be, therefore, catalytically reformed to increase aromatics content and used as an alternative component to automotive gasoline or as a valuable source of BTEX hydrocarbons.

The kerosene fraction was a major component of the hydrotreated STPO creating over 40 wt%. Its aromatics content was reduced from 48.6 to 33.2 wt% at 360 °C and 10 MPa. To produce high-quality drop-in jet fuel, mild hydrogenation or blending with non-aromatic HEFA bio-fuel can be applied.

The diesel fractions (almost 60 wt% of hydrotreated products) obtained at 330 and 360 °C and 10 MPa can potentially become an alternative component of diesel fuel. The higher density and aromatics content and accompanying lower cetane number can be improved by blending with HVO biofuel in a 65:35 mass ratio to obtain excellent quality drop-in diesel fuel (CFPP below –38 °C).

The bottom residue has the potential to be utilized as a high-quality component of bunker-type ultra and very low sulfur fuel oil used for marine transportation. It could also be co-hydrocracked with a common fossil residual feedstock to increase the yield of favored gasoline and middle distillates.

After the 170 h of STPO hydrotreating at both pressures tested, no loss in the catalyst activity was observed. However, much less coke was formed on the catalyst surface at 10 MPa.

We demonstrated that STPO could be used as a feedstock to produce alternative components of transportation fuels if a common hydro-treating catalyst at 360 °C and 10 MPa is applied. Obtained results point to the fact that the STPO is a perspective feedstock for being used in oil refinery schemes with high carbon utilization and waste management capabilities.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: [Petr Straka reports financial support was provided by Technology Agency of the Czech Republic. Petr Vozka reports financial support was provided by Center of Research Excellence in Science and Technology (CREST) Center for Energy and Sustainability (CEaS).].

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2023.141764>.

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