



Waste-derived fuel from tire pyrolysis oil hydrotreating: Insight into the transformation of heavy compounds and heteroatom removal

Downloaded from: <https://research.chalmers.se>, 2026-10-30 06:48 UTC

Citation for the original published paper (version of record):

Lê, X., Nguyen, M., Rehn, E. et al (2026). Waste-derived fuel from tire pyrolysis oil hydrotreating: Insight into the transformation of heavy compounds and heteroatom removal. *Fuel Processing Technology*, 292. <http://dx.doi.org/10.1016/j.fuproc.2026.108607>

N.B. When citing this work, cite the original published paper.



Waste-derived fuel from tire pyrolysis oil hydrotreating: Insight into the transformation of heavy compounds and heteroatom removal

Huy Xuan Le^a, Tung Manh Nguyen^a, Emma Rehn^a, Phuoc Hoang Ho^{a,1}, Quoc Khanh Tran^{a,2}, Olov Öhrman^b, Derek Creaser^a, Louise Olsson^{a,*}

^a Chemical Engineering Division, Competence Centre for Catalysis, Chalmers University of Technology, Gothenburg 412 96, Sweden

^b VAROPreem, Gothenburg SE-418 23, Sweden

ARTICLE INFO

Keywords:

Tire pyrolysis oil
Catalytic hydrotreatment
Hydrodesulfurization
Olefin saturation
Renewable fuel

ABSTRACT

Pyrolysis offers a promising route for valorization of waste tires. However, waste tire pyrolysis oil (WTPO) contains high concentrations of heteroatoms, limiting its direct use as a fuel. In this study, the transformation of WTPO fractions and representative compound groups during hydrotreating was investigated under a range of operating conditions. Temperature was identified as a key factor controlling the balance between hydrogenation and thermal cracking. At lower temperature hydrogenation was effective, whereas depolymerization and cracking increased substantially at 380 °C and above. The reactivity of gum-forming olefinic compounds depended strongly on molecular structure. Terminal and conjugated olefins were readily hydrogenated, while internal olefins required more hydrogen-rich conditions for effective stabilization. Sulfur speciation analysis showed that hydrodesulfurization (HDS) activity was governed by aromaticity and steric effects, with thiophenic compounds exhibiting higher reactivity than bulkier dibenzothiophenes. Effective upgrading was achieved at 360 °C using a catalyst-to-WTPO ratio of 8:75, providing strong hydrogenation activity while minimizing cracking. Under these conditions, a 96.7 wt% liquid yield, near-complete olefin removal, and 63% HDS were obtained. The catalyst also exhibited stable performance over multiple cycles, with negligible deactivation following recalcination. These findings provide mechanistic insights and practical guidance for efficient WTPO upgrading to high-quality fuel products.

1. Introduction

The global demand for transportation has increased in parallel with the rapid expansion of global markets. This growth in vehicle manufacturing has driven a significant rise in tire production and, consequently, the generation of large volumes of waste tires. According to the European Tyre & Rubber Manufacturers' Association, approximately 4.5 million tons of scrap tires were discarded in Europe in 2024

[1]. Of this total, only about 600 thousand tons were properly treated, meanwhile the remainder ended up in landfills. Tires are primarily composed of rubber, along with carbon black, additives, and inorganic fillers [2], and they require more than a century to fully decompose. Accumulated waste tires occupy substantial landfill space, creating breeding grounds for disease-carrying insects and rodents, in addition to increasing the risk of fires [3–5]. Furthermore, discarded tires release contaminants into the environment, leading to groundwater and soil

Abbreviations: WTPO, Waste tire pyrolysis oil; HDS, Hydrodesulfurization; HDN, Hydrodenitrogenation; HDO, Hydrodeoxygenation; GCxGC–MS–FID, Two-dimensional gas chromatography coupled with Mass Spectrometry and Flame Ionization Detector; GC–SCD, Gas chromatography coupled with Sulfur Chemiluminescence Detector; ICP–SFMS, Inductively coupled Plasma-sector field Mass spectroscopy; TGA, Thermogravimetric analysis; NMR, Nuclear magnetic resonance; TAN, Total acidity number; HHV, Higher heating value; PXRD, Powder X-ray diffraction; SEM/EDX, Scanning electron microscopy/Energy dispersive X-ray spectroscopy; NP, Naphtha (< 177 °C); MD, Middle distillate (177–343 °C); VGO, Vacuum gas oil (343–524 °C); DDS, Direct desulfurization; HYD, Hydrogenation; HDT, Hydrotreating; H_{aromatic}, Aromatic hydrogen; H_{olefinic}, Olefinic hydrogen; H_{paraffinic}, Paraffinic hydrogen.

* Corresponding author.

E-mail address: louise.olsson@chalmers.se (L. Olsson).

¹ Present address: Faculty of Chemical Engineering, Ho Chi Minh City University of Technology, and Vietnam National University Ho Chi Minh City, Ho Chi Minh City, Vietnam.

² Present address: Institute of Energy and Technology - Electrochemical Process Engineering (IET-4), Julich Research Center, Julich 524 28, Germany

<https://doi.org/10.1016/j.fuproc.2026.108607>

Received 2 July 2026; Received in revised form 7 September 2026; Accepted 22 September 2026

Available online 6 October 2026

0378-3820/© 2026 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

pollution by heavy metals and toxic chemicals [6]. Given these significant environmental impacts, the development of sustainable and cost-effective recycling strategies for waste tires has become a major concern worldwide.

Pyrolysis has emerged as a sustainable pathway for waste tire valorization [7]. At a high temperature ranging from 300 to 550 °C, waste tires can be converted into oils, carbon black, and steel [8]. Waste tire pyrolysis oil (WTPO) is the primary fraction, which accounts for 40–50 wt% of total products [3]. Compared with similar oils derived from biomass, WTPO offers the advantage of a superior energy density, approaching that of diesel fuel [9,10]. However, its high viscosity and low flash point prevent WTPO from being used directly as a conventional fuel [11,12]. The high olefin content contributes to instability, causing pipeline clogging or other storage issues [13]. Furthermore, the presence of heteroelements like sulfur and nitrogen, along with polyaromatic compounds, causes air pollution and risks to combustion engine performance [12]. Hence, in recent years, the upgrading of WTPO has received significant attention from both industry and scientists over the world.

Hydrotreatment has emerged as an effective technique for the valorization of WTPO [3]. This process removes undesirable heteroatoms through catalytic reactions such as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO). These reactions occur via the interaction of heteroatom-containing compounds with hydrogen under elevated temperatures and pressures. In addition to heteroatom removal, hydrotreatment promotes the saturation of olefinic and polyaromatic species, thereby improving the stability and overall quality of the upgraded oil. Transition metal-based catalysts are commonly used to enhance the efficiency of WTPO upgrading [14]. Compared with non-catalytic hydrotreatment, the use of a catalyst enhances product selectivity and upgrading efficiency under milder operating conditions, thereby improving the economic viability and operational performance of the process [15]. Jantaraksa et al. [16] reported an HDS efficiency of 87.8% during batch mode hydrotreatment of WTPO diluted in decane using a NiMo/Al₂O₃ catalyst. Catalyst loading, hydrogen pressure, reaction time, and temperature are important operating parameters strongly influencing removal effectiveness. Kingputtpong et al. [17] investigated the promotional effects of molybdenum (Mo), tungsten (W), and platinum (Pt) on the catalytic performance of Ni/Al₂O₃, finding that NiMo/Al₂O₃ provided the highest HDS activity due to its superior sulfur tolerance and acidity. In parallel, co-processing WTPO with other feedstocks such as vegetable oil [18], light cycle oil [19,20], waste engine oil [21], and tetralin [22] has also been found to benefit hydrotreating performance, resulting in lower coke formation and more efficient heteroatom removal.

Despite notable progress in WTPO hydrotreatment, previous studies using conventional sulfided NiMo/Al₂O₃ hydrotreating catalysts have focused primarily on heteroatom-removal efficiency. The present study therefore investigates both the chemical transformations occurring during WTPO hydrotreatment and the sulfur removal using a NiMo/Al₂O₃ catalyst. We have for the first time, according to our knowledge, showed a comparison of the individual boiling-point fractions and compound groups under different reaction conditions during WTPO upgrading, which is essential for evaluating the potential production of fuel-range products. Sulfur speciation in both the feed and upgraded oil was analyzed by GC-SCD, while hydrogen uptake under different reaction conditions was quantified using material-balance calculations based on elemental analysis. Furthermore, nuclear magnetic resonance (NMR) spectroscopy was employed to examine changes in functional groups, and for the first time, correlate different olefin types with the fuel instability. Finally, the regeneration behavior of the NiMo/Al₂O₃ catalyst was assessed, which has not been previously presented for WTPO upgrading at high hydrogen pressure.

2. Experimental

2.1. Materials

The crude WTPO was supplied by VAROPreem and originated from a demonstration-scale plant. Nickel(II)nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 99.999%) and ammonium tetramolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, 99.98%) were obtained from Sigma-Aldrich and used as metal precursors for catalyst synthesis. Gamma-alumina (γ-Al₂O₃, PURALOX) serving as the support material was received from Sasol Limited (Germany). High-purity hydrogen gas (99.999%) was utilized as the reducing agent during catalyst activation and performance evaluation. Additionally, a gas mixture containing 2.0 vol% oxygen in argon was used for catalyst passivation. All gases used in this study were supplied by Linde (Sweden). Unless otherwise specified, all chemicals were used as received without any further purification.

2.2. Catalyst preparation of NiMo/Al₂O₃

The catalyst was prepared using an incipient wetness impregnation method. Prior to impregnation, γ-Al₂O₃ was first calcined at 450 °C for 6 h. Pre-determined amounts of Ni(NO₃)₂·6H₂O and (NH₄)₆Mo₇O₂₄·4H₂O were dissolved in an appropriate volume of Milli-Q water and then added dropwise to the support material. The molar ratio of Ni/(Ni + Mo) was maintained at 0.33, corresponding to 2.3 wt% Ni and 8.0 wt% Mo. The impregnated material was dried overnight at 80 °C in an open crucible and subsequently calcined in air, also in an open crucible, at 450 °C for 6 h to yield the NiMo/Al₂O₃ catalyst. Before the hydrotreating experiments, the catalyst was activated at 450 °C for 5 h with 20 bar H₂ (room temperature). The activated catalyst was then flushed several times with inert nitrogen at room temperature to remove residual hydrogen. To prevent uncontrolled oxidation and enable safe handling, the reduced catalyst was passivated using 2.0 vol% O₂ in argon before exposure to air and subsequent use in the reaction.

2.3. WTPO hydrotreating experiments

Catalytic upgrading of WTPO was conducted in a 300 mL Parr high-pressure autoclave reactor. In a typical experiment, 75 g WTPO and a specific amount of catalyst were charged into the reactor, which was then sealed and purged three times with nitrogen, followed by three purges with hydrogen. After purging, the hydrogen pressure was adjusted to 40 bar at 25 °C. For all experiments, the liquid phase was stirred at 900 rpm throughout the entire reaction period. The reactor was subsequently heated to the target temperature at an average rate of 8 °C·min⁻¹, with the reaction time defined as zero at the point when the set temperature was reached. Temperature was controlled using a PID-controlled heating jacket with a precision of ±1 °C. At the end of the reaction, the reactor was cooled to room temperature and depressurized. This was followed by flushing the reactor three times with nitrogen before opening the vessel. Mass changes were monitored by weighing the reactor before and after each run. The liquid product was separated from the reaction mixture via vacuum filtration through a 4 μm glass filter (ROBU, Germany). The remaining solid residue, consisting of catalyst and possible coke, was thoroughly washed with acetone, dried at 80 °C overnight, and weighed. For experiments involving periodic hydrogen replenishment, the same procedure was followed, except the hydrogen pressure was replenished to 70 bar every 15 min.

2.4. Product analysis

The mass distributions of the different product fractions obtained during upgrading were calculated using Eqs. (1–3):

$$Y_G (\text{wt}\%) = \frac{m_{\text{reactor (initial)}} - m_{\text{reactor (post-reaction)}}}{m_{\text{WTPO}}} \times 100\% \quad (1)$$

$$Y_S (\text{wt}\%) = \frac{m_{\text{solid residue}} - m_{\text{catalyst}}}{m_{\text{WTPO}}} \times 100\% \quad (2)$$

$$Y_L (\text{wt}\%) = 100 - Y_G - Y_S \quad (3)$$

Where:

- Y_G, Y_S, Y_L are the yields of gas, solid, and liquid products, respectively, after WTPO upgrading.
- $m_{\text{reactor (initial)}}, m_{\text{reactor (post-reaction)}}$ are the masses of the autoclave, including feedstock, liquid products and catalyst, before and after the reaction, respectively.
- $m_{\text{catalyst}}, m_{\text{solid residue}}$ are the masses of the applied catalyst and the solid recovered after thoroughly washing with acetone, respectively.
- m_{WTPO} is the feed mass of WTPO.

The liquid products obtained were analyzed using a two-dimensional GCxGC-MS-FID (7890B-5977A, Agilent) instrument equipped with a flow modulator. Detailed information on the instrumental configuration and analytical procedure can be found in the Supplementary Information (SI), **Section S1**. All the peaks detected using GC Image software were included in the determination of the GC-detectable liquid yield. The GC-detectable species were quantified by group-type analysis based on peak volumes, using internal standard calibration method with representative response factors for each compound subgroup. The quantified subgroups were then summed to obtain the total GC-detectable yield, which was calculated according to Eq. (4):

$$\text{GC detectable yield (wt}\%) = \frac{\text{Total amount of detected components (g)}}{\text{Amount of analyzed oil sample (g)}} \times 100\% \quad (4)$$

The concentration of sulfur in oils was determined by Inductively Coupled Plasma-Sector Field Mass Spectrometry (ICP-SFMS, ALS Scandinavia AB, Luleå, Sweden). The hydrodesulfurization efficiency was calculated from the difference in sulfur content between the feedstock and the hydrotreated products, according to Eq. (5):

$$\text{HDS efficiency (\%)} = \frac{C_f - C_p}{C_f} \times 100\% \quad (5)$$

Where C_f and C_p are the sulfur contents in feedstock and product, respectively. The sulfur components in the original WTPO and one hydrotreated sample with the best upgrading performance were examined by GC-SCD (SGS United Kingdom Limited, Middlesbrough, UK), see **Section S1** in Supplementary Information (SI) for further information. Other impurity conversions, including hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO), were calculated analogously to the HDS efficiency, using Eq. (5), where C_f and C_p denote the contents of respective impurities in the feedstock and product. These impurity contents were directly determined by elemental analysis.

Hydrogen consumption was calculated using the elemental composition and ICP-SFMS data for both the feedstock and product oils. This method is adapted from Zhang et al. [23], with the modification that changes in oxygen content are also included. As detailed in the Supplementary Information (SI), the calculation is based on elemental material balances, assuming that sulfur (S), nitrogen (N), and oxygen (O) are removed as H_2S , NH_3 , and H_2O , respectively. The final equation for hydrogen consumption (g H_2 per kg WTPO) is:

$$\begin{aligned} \text{H}_2 \text{ consumption (g H}_2 \cdot \text{kg WTPO}^{-1}) &= 10 \times \left[\frac{C_f}{C_p} \times H_p - H_f + \frac{1}{16} \right. \\ &\quad \times \left(S_f - \frac{C_f}{C_p} \times S_p \right) \times 10^{-4} + \frac{3}{14} \\ &\quad \times \left(N_f - \frac{C_f}{C_p} \times N_p \right) + \frac{1}{8} \times \left(O_f - \frac{C_f}{C_p} \times O_p \right) \left. \right] \end{aligned} \quad (6)$$

Where C_f and H_f represent the carbon (C) and hydrogen (H) contents (wt%) of the feedstock, while C_p and H_p denote the corresponding contents in the product oil. The N and O contents (wt%) in the crude WTPO are given as N_f and O_f , and contents in the hydrotreated oil are denoted by N_p and O_p . Sulfur contents (mg/kg) in WTPO and upgraded products, obtained from ICP-SFMS analysis, are represented as S_f and S_p , respectively. The derivation of Eq. (6) can be found in the Supplementary Information (SI), **Section S2**. Additional analytical methods were used to characterize the oil products, including elemental analysis, thermogravimetric analysis (TGA), proton and phosphorus-31 nuclear magnetic resonance spectroscopy (^1H and ^{31}P NMR), volumetric Karl-Fisher titration, and carbonyl content determination. Details of these product analyses are provided in **Section S1** of the Supplementary Information.

2.5. Catalyst characterization

Powder X-ray diffraction (PXRD) patterns were collected using a Bruker D8 diffractometer equipped with a Cu K α monochromatic radiation source ($\lambda = 1.542 \text{ \AA}$). Data were recorded over a scanning angle (2θ) range of 10 to 80° , with a step size of 0.03° and a dwell time of 1 s. Catalyst morphology and metal distribution were examined by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDX) using a JEOL JSM-7800F Prime operated with an accelerating voltage of 15 kV. Textural properties of the support and as-synthesized catalyst were determined by N_2 physisorption at -196°C employing a Micrometrics TriStar 3000 instrument. The specific surface area and average pore size were calculated by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively, and the micropore volume was determined based on the t-plot method. Metal loading in the catalyst was measured by ICP-SFMS (ALS Scandinavia AB, Luleå, Sweden).

3. Results and discussion

3.1. Material characterizations

3.1.1. Catalyst characterization

The XRD patterns of the $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst and $\gamma\text{-Al}_2\text{O}_3$ support are displayed in Fig. 1a. Both materials exhibit the characteristic 2θ reflections of $\gamma\text{-Al}_2\text{O}_3$, identical to the reference pattern (PDF#29-0063). Despite the relatively high total metal loading (10 wt %), the diffraction pattern of $\text{NiMo}/\text{Al}_2\text{O}_3$ closely resembles that of the support. No other peaks corresponding to crystalline NiO (PDF#44-1159) or MoO_3 (PDF#05-0508) were detected. This indicates that Ni and Mo species are either well-dispersed on the alumina support, present as oxide crystallites with sizes below the XRD detection limit, or present at concentrations insufficient for detection by XRD [24].

Fig. 1b presents the N_2 physisorption isotherms, and the corresponding textural properties derived from the isotherms are summarized in Table 1. Both the γ -alumina support and $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst exhibit type-IV adsorption isotherms, characteristic of mesoporous structures according to the IUPAC classification [25]. The type-H2 hysteresis loop indicates a complex neck-like pore system with a broad neck size distribution. Compared with the bare support, the as-synthesized catalyst shows a pronounced decrease in both specific surface area and pore volume. This reduction is likely due to the penetration of the metal

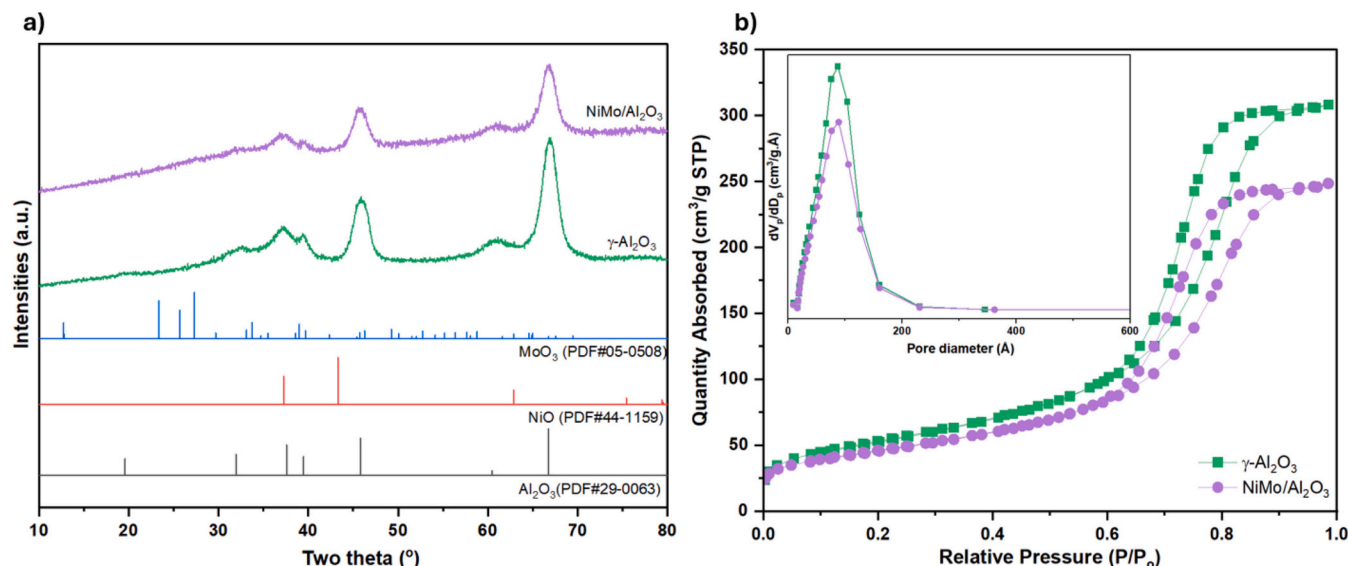


Fig. 1. XRD patterns (a) and nitrogen adsorption-desorption isotherms with pore diameter distribution (b) of alumina support and NiMo/Al₂O₃ catalyst.

Table 1

Textural properties of γ -Al₂O₃ and NiMo catalyst derived from ICP and N₂ physisorption measurements.

	Metal loading by ICP (wt%)		Specific surface area (A, m ² /g)	Total pore volume (V _p , cm ³ /g)
	Ni	Mo		
γ -Al ₂ O ₃	–	–	192.6	0.48
NiMo/Al ₂ O ₃	2.5	7.3	165.4	0.39

species into the pore network of γ -Al₂O₃, implying successful impregnation of the metals. Despite this decrease, the calcined NiMo/Al₂O₃ catalyst retains a relatively high specific surface area and pore volume, which should allow effective diffusion and be beneficial for WTPO upgrading reactions.

The morphology and metal distribution of the synthesized NiMo/Al₂O₃ catalyst were examined by SEM-EDX, and the results are shown in Fig. 2. The catalyst exhibited an inhomogeneous surface structure with regions of aggregated crystals, which may have formed due to the growth of active metal species during the impregnation process. EDX elemental mapping further confirmed that the metal dopants were uniformly dispersed throughout the alumina support.

3.1.2. Physicochemical properties of waste tire pyrolysis oil

The physicochemical properties of the WTPO employed in this study are provided in Table 2. WTPO is a complex mixture of hydrocarbons, with a low ash content. The water content was only 0.32 wt%, which is considerably lower than that typically found in bio-oils derived from lignocellulosic biomass, where water is often a significant problem [26]. WTPO showed a TAN of 3.33 mg KOH/g, implying the presence of oxygenated polar compounds [27]. This observation is consistent with the hydroxyl number determined by ³¹P NMR, which showed only low concentrations of OH-containing functional groups. The carbonyl content of WTPO was 2.67 mg CO/g, comparable to that of conventional transportation fuels [18]. Its H/C molar ratio of 1.53, suggests a mixture enriched in paraffinic and aromatic compounds [28]. WTPO also exhibited a relatively high higher heating value (HHV) of 42.9 MJ/kg, underscoring its potential for energy applications; this value is close to that of commercial gasoline (47 MJ/kg) and diesel (45 MJ/kg) [29]. GCxGC-MS analysis revealed that WTPO is predominantly composed of

aliphatic hydrocarbons and olefins, with limonene identified as the most abundant compound, consistent with previous studies [14,27]. Additionally, single-ring aromatics (e.g., BTEX, cymene), polycyclic aromatics (such as indene and naphthalene derivatives), cyclic compounds, and various aliphatic derivatives are also found in the WTPO mixture (Table S6).

According to the TGA SimDist analysis, the feedstock can be divided into three fractions based on their boiling ranges: naphtha (NP, IBP–177 °C), middle distillate (MD, 177–343 °C), and vacuum gas oil (VGO, 343–524 °C). No residue (> 524 °C) was detected in the WTPO. Among these fractions, MD was the most abundant, accounting for 57.5 wt%. Elemental analysis revealed relatively high concentrations of heteroatoms – nitrogen (0.59 wt%), oxygen (0.76 wt%), and particularly sulfur (0.82 wt%) – likely originating from the thermal degradation of vulcanization agents and accelerators used in tire manufacturing [30]. According to literature, nitrogen-containing species in WTPO primarily include aniline, benzothiazole, long-chain nitriles, and quinoline derivatives [31], while organosulfur compounds are commonly found as thiophene, benzothiazole, and benzothiophene derivatives [29]. Oxygenated compounds are less abundant than other heteroatom-containing species and mainly occur as organic acids, phenols, ketones, and alcohols [27].

3.2. Effects of operating parameters on WTPO upgrading

3.2.1. Effect of reaction temperature

The effect of reaction temperature in the range of 340–400 °C on WTPO hydrotreating was investigated. As the temperature increased, the liquid yield gradually decreased, while the gas yield increased correspondingly. As shown in Fig. 3a, the distribution of product fractions based on TGA measurements remained largely unchanged for the feedstock and experiments performed at 340 and 360 °C. However, at higher temperatures, a clear conversion of the heavy fraction was observed: the VGO content decreased significantly from 20.3 wt% to 15.5 wt% and 13.7 wt% at 380 °C and 400 °C, respectively. Simultaneously, the naphtha fraction increased from 22.2 wt% to 29.7 wt%. In contrast, the most valuable middle-distillate fraction declined slightly, from 57.5 wt% to 53.8 wt% at 400 °C. These results indicate that high temperature promote cracking reactions, which can negatively impact the quality and distribution of the upgraded products. Notably, no coke formation was detected under any of the investigated conditions, highlighting the favorable potential for large-scale operation with WTPO.

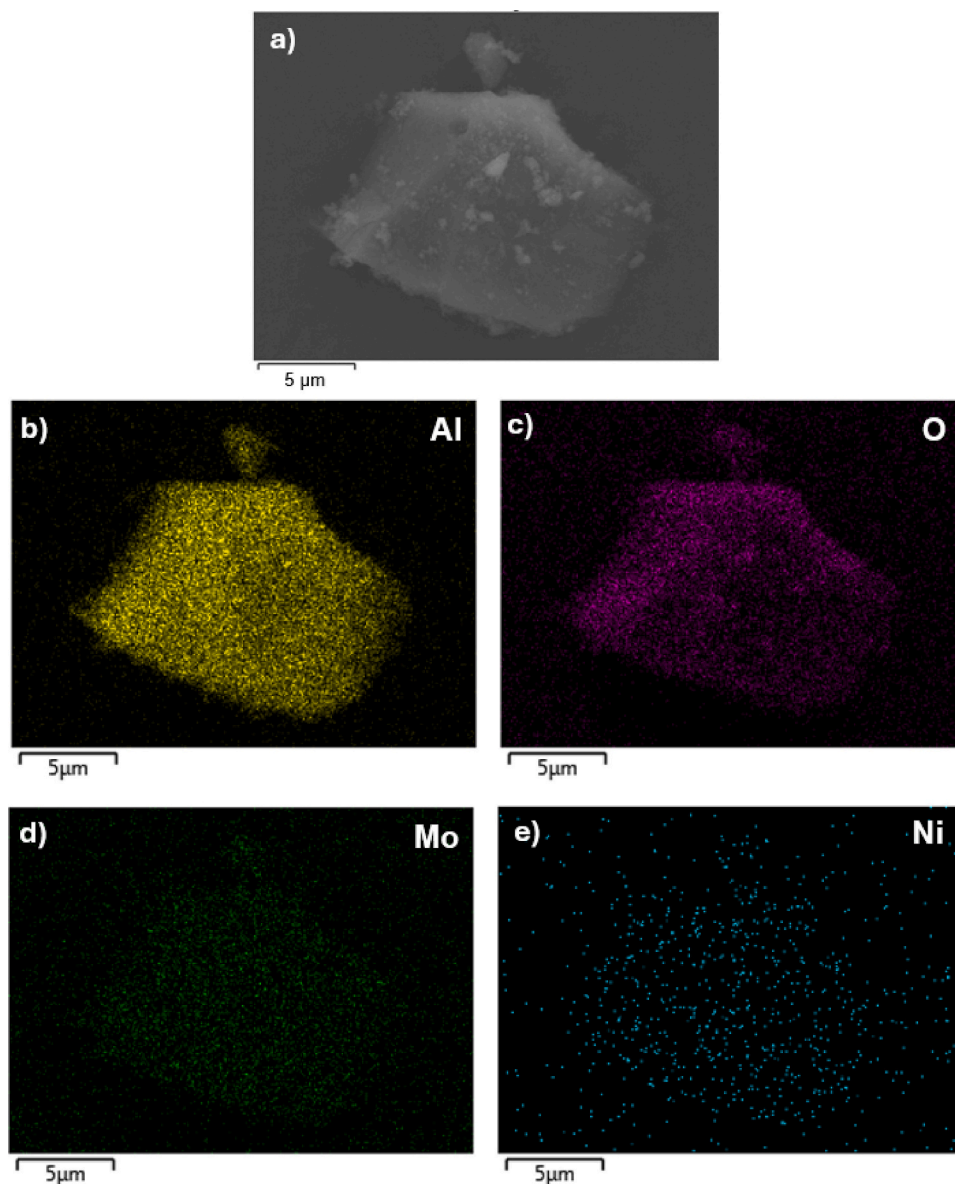


Fig. 2. SEM images of (a) NiMo/Al₂O₃ and (b-e) its EDX dot-mapping.

Fig. 3b illustrates the distribution product compound types as a function of reaction temperature based on GCxGC-MS analysis. Six major compound classes were identified: monocycloalkanes, monoaromatics, olefins, aliphatics, polycycloalkanes, and polyaromatics, which is consistent with the findings of Straka et al. [33]. It is worth noting that compounds not detected by GC are assumed to be heavier species that cannot be volatilized in the GC inlet. The proportion of GC-detectable products increased markedly from 58.2 wt% in the feed to 99.8 wt% in the liquid product obtained at 400 °C, indicating a significant shift toward lower-boiling compounds as a result of hydrocracking. The increase in GC-detectable yield indicates that a larger fraction of the WTPO was converted into compounds sufficiently volatile and detectable by GCxGC-MS, consistent with the transformation of larger macromolecules into smaller compounds through cracking reactions [34]. In parallel, the overall increase in polycycloalkanes and monocycloalkanes indicates that hydrogenation occurred simultaneously with cracking under these conditions. GCxGC-MS analysis of the C₁₀H₁₆ hydrogenation products (Fig. S1a) shows their stepwise transformation to C₁₀H₁₈ and C₁₀H₂₀ at lower temperatures, showing hydrogenation occurs during WTPO hydrotreatment in this temperature range. However, at

400 °C, the total abundance of these C₁₀ species increased markedly, suggesting that cracking of larger molecules contributes to additional C₁₀-range products at this temperature. This interpretation is consistent with previous studies, showing a transition temperature region between hydrogenation and cracking regimes with similar feedstocks [35,36]. This interpretation is further supported by the increased proportion of aliphatics as the reaction temperature rose. Within the 340–380 °C range, only a modest increase in the GC-detectable yield was observed, whereas a pronounced enhancement was seen at 400 °C. These findings demonstrate that WTPO conversion is highly sensitive to temperature: hydrogenation is effective at lower temperature (340 and 360 °C), consistent with the nearly unchanged TGA-based boiling-point distribution, whereas above 400 °C, catalytic thermal depolymerization becomes much more significant, yielding 99.8% GC-detectable compounds. The temperature dependence of WTPO upgrading is further supported by the evolution of the BTEX (benzene-toluene-ethylbenzene-xylene) content (Fig. S1b), which shows a remarkable increase in the yields of benzene, toluene, ethylbenzene, and xylenes in the hydro-treated product at 400 °C. This increase indicates the enhanced conversion of large molecules into smaller aromatic compounds at higher

Table 2
Physico-chemical properties of WTPO.

Properties	Value	Used method
Appearance	Dark brown, viscous liquid	
Ash content (wt.%)	< 0.02	ASTM D482-19
Water content (wt.%)	0.32 ± 0.01	ASTM D6304-20
TAN (mg KOH/g)	3.33 ± 0.13	Modified ASTM D664-18
Carbonyl content (mg CO/g)	2.67 ± 0.41	Modified Faix method
Hydroxyl functional groups		³¹ P NMR
Carboxylic acid OH (mmol/g WTPO)	0.097	
Phenolic OH (mmol/g WTPO)	0.127	
Aliphatic OH (mmol/g WTPO)	0.166	
Elemental analysis		
Carbon (wt.%)	85.93 ± 0.42	
Hydrogen (wt.%)	10.94 ± 0.20	
Nitrogen (wt.%)	0.59 ± 0.01	
Oxygen (wt.%)	0.76 ± 0.01	
H/C molar ratio	1.53	
Sulfur (wt.%)	0.82	ICP-SFMS
HHV (MJ/kg)	42.9	Channiwalla and Parikh [32]
Boiling point distribution		TGA SimDist
Naphtha (wt.%, IBP–177 °C)	22.2	
Middle distillate (wt.%, 177–343 °C)	57.5	
Vacuum gas oil (wt.%, 343–524 °C)	20.3	
Residue (wt.%, > 524 °C)	0	

temperatures. To further investigate the transformation pathways of WTPO during hydrotreating, additional analysis was conducted at an intermediate temperature of 360 °C, which provided the highest middle-distillate yield (Fig. 3a), while limiting cracking to only 2.1 wt% gas formation.

¹H NMR analysis was used to monitor changes in the chemical composition of the feedstock during hydrotreating. The full spectra are provided in Fig. S2–S4. Protons corresponding to aromatic, olefinic, α -side-chain, naphthenic, and paraffinic regions were identified within the chemical shift ranges 9.00–6.43, 6.20–4.50, 4.00–2.00, 2.00–1.57,

and 1.57–0.25 ppm, respectively [37]. The relative abundance of each hydrocarbon type was calculated from the integrated areas of these regions, normalized to the total integrated area of the spectrum; the results are summarized in Table 3. In the WTPO feedstock, paraffinic and naphthenic hydrogens constituted the dominant proton types, consistent with the considerable contribution of limonene. Limonene contains paraffinic side-chains attached to a naphthenic ring structure [6,14], and its presence in WTPO was confirmed by GCxGC-MS at 6.5 wt%.

An increase in operating temperature resulted in higher proportions of $H_{aromatic}$ and $H_{paraffinic}$, indicating enhanced removal of side chains or alkyl bridges from aromatic compounds followed by hydrogen termination of the resulting radicals. Zhen et al. [38] observed a similar trend, with progressive C–C bond cleavage in the side chains of aromatic species within the 300–400 °C range. This behavior aligns with the results in Fig. 3b, where an increase in monoaromatic species was observed. In contrast, $H_{olefinic}$ showed a distinct pattern, it decreased steadily up to 380 °C but showed a slight increase at 400 °C. These results suggest that hydrogenation becomes more dominant as the temperature increases to 380 °C, while at 400 °C cracking and depolymerization reactions intensify substantially, consistent with the GCxGC-MS results (Fig. 3b).

3.2.2. Effect of reaction time

The transformation of different fractions and compound classes in the feedstock during hydrotreating was evaluated by analyzing oil products obtained at various residence times at 360 °C. The results are presented in Fig. 4. Across all residence times, the total liquid yield remained high – around 98 wt% – with a corresponding gas yield of approximately 2.3 wt% (Fig. 4a). However, the overall boiling point distribution changed only slightly, a gradual increase in lighter fractions was observed over time, consistent with the findings reported by Badoga et al. [39]. After 4 h, a modest reduction in the heavier fractions was observed, in which the VGO fraction decreased from 20.3 wt% to 17.5 wt%, and the MD fraction declined from 57.5 wt% to 53.9 wt%. This behavior aligns with literature reports highlighting the reactivity of heavy components during hydrotreating of both fossil and bio-oils [40–42]. Notably, the amount of MD – considered the most valuable fuel fraction – obtained after 4 h at 360 °C was comparable to that produced after 1 h at 400 °C. However, VGO conversion after 4 h at 400 °C reached

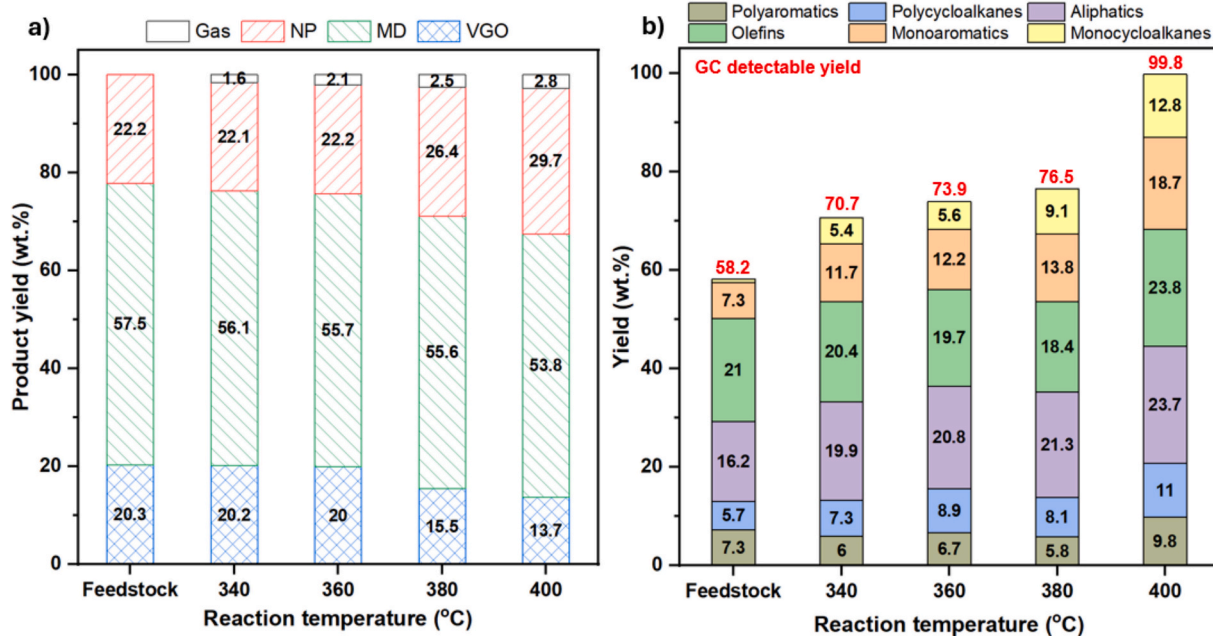


Fig. 3. Product distribution from TGA analysis (a) and chemical composition of GC-detectable fraction (b) for WTPO and hydrotreated products over NiMo/Al₂O₃ at different reaction temperatures. Reaction condition: initial H₂ pressure 40 bar, 75 g WTPO, catalyst-to-WTPO ratio 1:75, 1 h.

Table 3

Relative abundance of hydrocarbon groups (%) from integrating ^1H NMR chemical shift regions for WTPO and upgraded products at varying reaction conditions.

	Aromatic	Olefinic	α -side chain	Naphthenic	Paraffinic
WTPO	8.9	4.4	16.0	16.8	54.1
Temperature ($^{\circ}\text{C}$) (*)					
340 $^{\circ}\text{C}$	9.0	3.1	15.3	14.4	58.2
360 $^{\circ}\text{C}$	9.2	2.1	16.5	13.6	58.6
380 $^{\circ}\text{C}$	9.3	1.7	16.2	12.7	60.1
400 $^{\circ}\text{C}$	9.8	1.9	16.1	11.9	60.3
Reaction time (h) (**)					
0.5 h	8.8	2.6	16.0	14.2	58.4
1 h	9.2	2.1	16.5	13.6	58.6
2 h	9.0	1.9	16.0	12.8	60.3
4 h	8.7	1.6	14.3	12.2	63.3
Catalyst/WTPO ratio (wt./wt.) (***)					
1:75	8.7	1.3	13.8	10.7	65.5
2:75	8.6	1.1	13.4	10.3	66.6
4:75	8.5	0.7	13.0	9.6	68.1
8:75	8.4	0.4	12.7	9.4	69.1

(*): initial H_2 pressure 40 bar, without H_2 replenishment, catalyst-to-WTPO ratio 1:75, 1 h.

(**): 360 $^{\circ}\text{C}$, initial H_2 pressure 40 bar, without H_2 replenishment, catalyst-to-WTPO ratio 1:75.

(***): 360 $^{\circ}\text{C}$, with H_2 replenishment at 70 bar, 4 h.

32.5% (from 20.3 wt% VGO in feedstock to 13.7 wt% in product after 1 h; Fig. 3a), substantially higher than the 13.8% VGO conversion achieved after 4 h at 360 $^{\circ}\text{C}$ (from 20.3 wt% VGO in feedstock to 17.5 wt% after 4 h at 360 $^{\circ}\text{C}$; Fig. 4a). These results indicate that operating at lower temperatures favors a higher yield of valuable product fractions while minimizing excessive cracking, in agreement with the conclusions of Kohansal et al. [43].

To gain deeper insight into the transformation of WTPO compounds, GCxGC-MS analysis was performed on upgraded oils collected at different reaction times. The evolution of six compound-groups, including polyaromatics, polycycloalkanes, aliphatics, olefins,

monoaromatics, and monocycloalkanes are displayed on Fig. 4b. As the reactions progressed, the overall GC-detectable yield increased from 58.2 wt% to 76.3 wt%, indicating that heavier compounds were depolymerized into smaller species capable of volatilizing in the GC inlet. However, compared with the strong temperature effect observed between 360 $^{\circ}\text{C}$ to 400 $^{\circ}\text{C}$, varying the reaction time had a much weaker influence on WTPO conversion. This observation aligns with the findings of Feng et al. [44], who also reported a minimal impact of residence time on oil composition. Among the compound groups, olefins – particularly those containing side-chain carbon-carbon double bonds – exhibited the most pronounced change, dropping from 21.0 wt% to 15.4 wt% after 4 h. In contrast, the proportions of mono- and polycycloalkanes, as well as aliphatics increased over the same period, confirming that olefins were rapidly hydrogenated and converted into their corresponding saturated cyclic and aliphatic compounds. Similar olefin transformations into n-alkanes, isoalkanes, and cycloalkanes during WTPO hydrotreatment were also reported by Straka et al. [33]. On the other hand, only minor changes were observed in the aromatic fractions, suggesting that these compounds require higher activation energies for conversion. This is supported by the findings of Canete et al. [13], who reported that hydrogenation of aromatic rings requires harsher conditions than the saturation of other unsaturated species.

The effect of reaction time was also examined using ^1H NMR (Table 3 and Figs. S2–S4). At the moderate reaction temperature of 360 $^{\circ}\text{C}$, olefin saturation was already evident in the early stages of hydrotreating. In contrast, the aromatic-bound hydrogen remained largely unchanged, indicating that under these conditions the hydrogenation of aromatic compounds was relatively ineffective. Consequently, only negligible changes were observed in the polyaromatic and monoaromatic fractions, as shown in Fig. 4b. With prolonged reaction time, slow cracking became apparent, leading to a gradual decrease in α -side chain and naphthenic hydrogen.

In summary, reaction time has a much smaller effect on WTPO upgrading than temperature, which is expected given the strong temperature dependence described by the Arrhenius equation [45]. At the relatively low temperature of 360 $^{\circ}\text{C}$, the conversion of heavy fractions progressed slowly with time. Consistent with the boiling point fractionation results, GCxGC-MS data indicated that easily hydrogenated compounds, such as olefins, were preferentially upgraded, while heavier

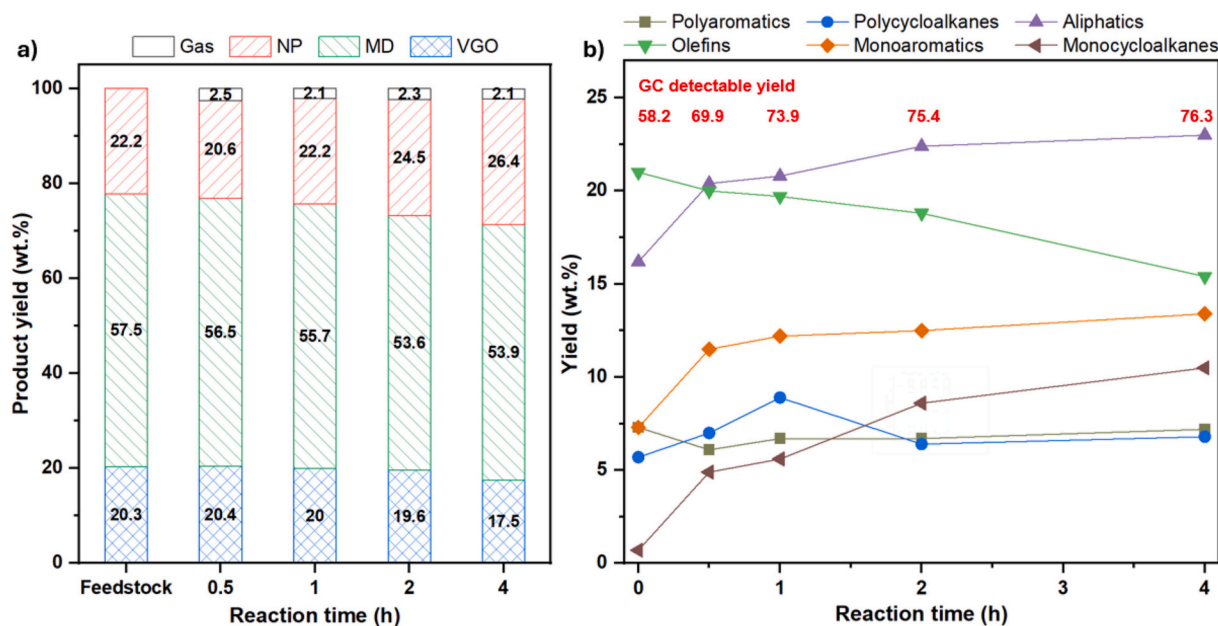


Fig. 4. Effect of reaction time on the product distribution based on TGA (a) and chemical composition of GC-detectable fraction (b) of WTPO and its hydrotreated products over NiMo/Al₂O₃ catalyst. Reaction condition: 360 $^{\circ}\text{C}$, initial H_2 pressure 40 bar, 75 g WTPO, catalyst-to-WTPO ratio 1:75.

aromatic compounds remained largely unchanged and would likely require more severe conditions to undergo hydrotreating reactions. In further work, subsequent investigations focused on another key operating parameter, namely hydrogen pressure.

3.2.3. Effect of hydrogen pressure

In the hydrotreating process, hydrogen plays a vital role in upgrading the feedstock. As the reaction proceeds, the partial pressure of hydrogen (P_{H_2}) gradually decreases, which can lead to hydrogen depletion and ultimately limit HYD activity. In addition, the reaction rate may increase with increasing hydrogen pressure, depending on the reaction kinetics. To investigate the effect of hydrogen availability, two experimental designs were used. The first run was carried out in batch mode under standard conditions at 360 °C for 4 h and an initial P_{H_2} of 70 bar. A second run was conducted under identical conditions, except that hydrogen was replenished to 70 bar every 15 min. A reference experiment under argon pressure (40 bar) without catalyst was also performed. The results are presented in Fig. 5.

As illustrated in Fig. 5a, the reaction carried out in an inert atmosphere produced a substantial gas yield, indicating more extensive cracking when hydrogen was absent. Interestingly, when comparing the feedstock with the Ar experiment (i), the olefin content still decreased from 21 to 16 wt% (Fig. 5b), despite the lack of external hydrogen. This suggests that some HYD activity occurred. Such hydrogenation was likely driven by natural hydrogen donors generated during WTPO thermolysis, such as substituted naphthenes in the heavy resid oil, which can act as internal hydrogen sources [46,47]. However, the overall upgrading efficiency under these conditions remained low, as the GC-detectable yield was nearly unchanged compared with the feedstock (Fig. 5b).

In contrast, the replenishment of hydrogen suppressed the generation of both gas and NP. When comparing the two hydrotreating experiments, heavier VGO and MD fractions were higher in H_2 -replenishment experiment (iii) than in the run without recharged H_2 (ii). In hydrotreating, both HYD and depolymerization/cracking are crucial processes. Cracking converts low-grade oil into lighter compounds and promotes heteroatom removal, improving fuel quality, while HYD saturates C=C bonds and other unsaturated functional groups containing heteroatoms such as nitrogen, sulfur, or oxygen, as well as trace metals

[48–50]. However, these reactions are known to compete [51]. In this study, the hydrogen top-up approach slowed the cracking/depolymerization of WTPO, as evidenced by the reduced formation of light products and correspondingly higher portions of heavy fractions. This observation is consistent with the decrease in GC-detectable yield to 70.1 wt% shown in Fig. 5b, indicating a lower conversion of macromolecules into smaller molecules. Further support for the suppression of cracking is provided by the observed decreases in aliphatics and monocycloalkanes in the hydrogen replenishment experiment.

3.2.4. Effects of catalyst loading

Besides the hydrogen pressure, the catalyst loading is another vital factor in the hydrotreating process. To evaluate its effect on WTPO upgrading, a series of experiments was conducted at 360 °C using catalyst-to-oil ratios ranging from 1:75 to 8:75 (wt./wt.). These ratios were adjusted by adding different amounts of catalyst to the reactor while keeping the WTPO mass constant. A reference experiment without catalyst was also conducted and is denoted as a catalyst-to-oil ratio of 0:75. In all experiments, hydrogen was periodically replenished to 70 bar at 15 min intervals to ensure sufficient hydrogen availability throughout the upgrading process.

As depicted in Fig. 6a, in the absence of a catalyst, the yields of light fractions such as gas and naphtha (NP) increased relative to the feedstock, indicating that thermal depolymerization and cracking occur under these conditions. The introduction of catalyst suppressed the gas formation and increased the liquid yield with a higher content of middle distillates. At a low catalyst-to-oil ratio of 1:75, the mass fraction of VGO decreased only slightly, from 20.3 wt% to 19.5 wt% (a 3.9% reduction) compared to the feedstock, demonstrating that this heavy fraction remains largely unreactive at such low catalyst loadings. This limited decrease reflects the overall low reactivity of WTPO under these conditions. Increasing the catalyst-to-oil ratio to 2:75 led to a substantial improvement, with the VGO fraction decreasing by 20.2% (from 20.3 wt% to 16.2 wt%), indicating markedly enhanced catalytic activity. Further increases in catalyst loading to 4:75 and 8:75 produced smaller additional gains in VGO conversion – 22.2% and 29.6% relative to the feedstock, respectively – indicating diminishing returns beyond a certain catalyst threshold. Similar suppression of thermal cracking/depolymerization of heavy fractions with increased catalyst loading has also

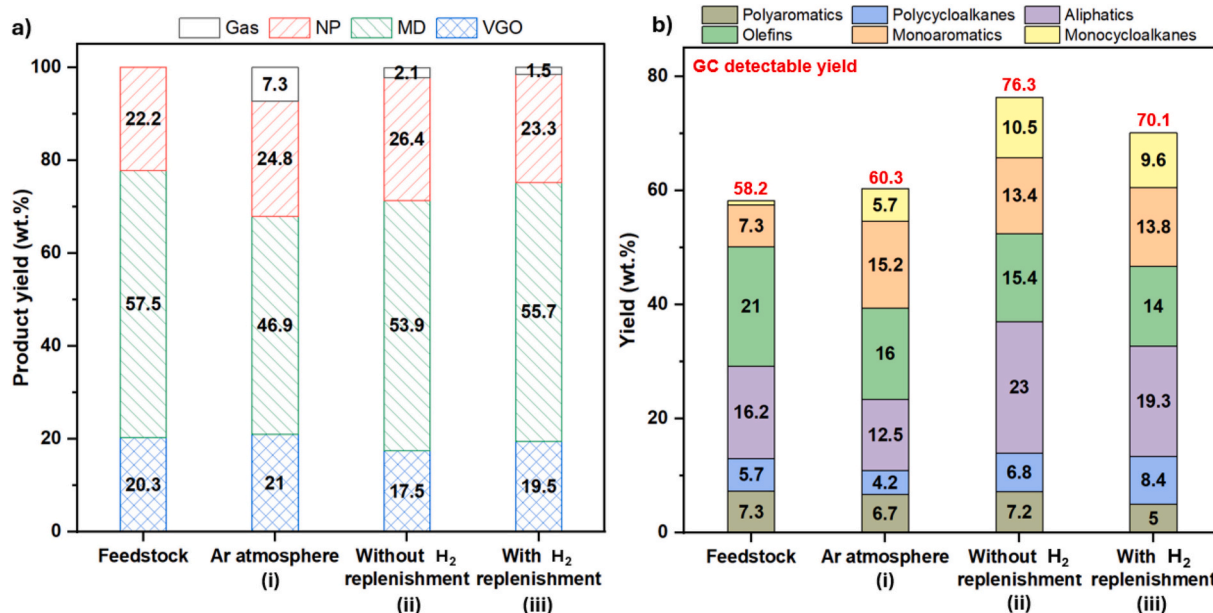


Fig. 5. The influence of hydrogen pressure on (a) product distribution from TGA and (b) chemical composition of GC-detectable fraction of WTPO and hydrotreated products over NiMo/Al₂O₃ catalyst. Reaction conditions: 360 °C, 75 g WTPO, 4 h. Experiments: (i) no catalyst, initial 40 bar Ar; (ii) catalyst-to-WTPO ratio 1:75, initial 40 bar H_2 without replenishment; (iii) catalyst-to-WTPO ratio 1:75, initial 40 bar H_2 with replenishment every 15 min to 70 bar.

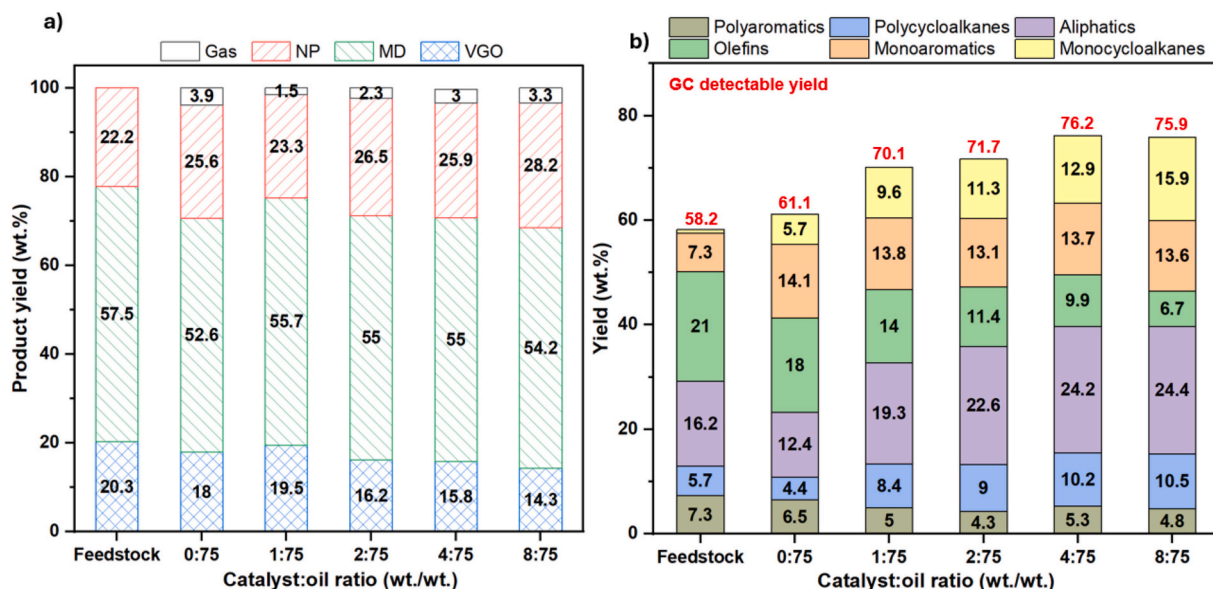


Fig. 6. Product distribution based on TGA (a) and chemical composition of GC-detectable fraction (b) of WTPO and its hydrotreated products over NiMo/Al₂O₃ catalyst at different catalyst-to-WTPO ratios. Reaction condition: 360 °C, topping-up H₂ every 15 min to 70 bar (360 °C), 75 g WTPO, 4 h.

been reported by Nguyen et al. [52].

The changes in chemical composition are summarized in Fig. 6b. Without catalyst, only a small portion of heavy fractions cracked into lighter products, as indicated by a modest increase in the GC-detectable yield from 58.2 to 61.1 wt%. Non-catalytic hydrotreatment produced a product with high abundance of aromatics and olefins, indicating limited hydrogenation in the absence of a catalyst. This observation is consistent with the findings of Summer et al. [53]. The addition of catalyst triggered hydrogenation and cracking reactions, leading to olefin saturation and an increase in the GC-detectable yield. These findings are consistent with the results of Yoon et al. [54] who reported improved cracking and hydrogenation activity with higher catalyst loading during the upgrading of waste-plastic pyrolysis oils. When the catalyst-to-oil ratio exceeded 4:75, the GC-detectable yield no longer improved. This observation suggests that at higher catalyst loadings, upgrading efficiency becomes limited by reaction kinetic rather than catalyst availability, consistent with the product distribution trends shown in Fig. 6a. The GC-detectable polyaromatic content changed only slightly with higher catalyst loading (Fig. 6b), reaching 4.8 wt% at the catalyst-to-oil ratio of 8:75 from 5.0 wt% for the catalyst-to-oil ratio of 1:75. On the other hand, the monocycloalkane content rose significantly, from 5.7 wt% to 15.9 wt% over the same catalyst-to-oil ratio range. This is expected, as the number of active sites increases with catalyst dosage, thereby facilitating more extensive saturation reactions [19,55]. Polyaromatics likely undergo partial hydrogenation, followed by bond cleavage, resulting in a reduced overall polyaromatic content and a corresponding increase in monocycloalkanes, which are most likely originating from hydrogenated monoaromatics. It should also be noted that a portion of the heavier polyaromatics is not detected by GC; as a result, the GC-detectable fraction remains nearly constant across different catalyst loadings. The experiment with top-up hydrogen was repeated three times and the results for TGA and GCxGC-MS are shown in Table S4. The results clearly show a high reproducibility.

The ¹H NMR data (Table 3 and Fig. S2-S4) showed a strong impact on the HYD reactions. The olefin content decreased substantially, along with a pronounced increase in paraffinic hydrogen. Moreover, the more refractory aromatics were gradually hydrogenated, leading to a clear decline in H_{aromatic}, which reached 8.4% at the catalyst-to-oil ratio of 8:75 (wt./wt.).

3.3. Sedimentation and gum formation

In the petroleum-derived products, excessive concentrations of olefins lead to polymerization, oxidation, and sediment formation during fuel transportation and storage [56]. During hydrotreating, terminal and unsubstituted branched olefins are preferentially hydrogenated, leaving substituted internal alkenes as the dominant olefin species in the upgraded products. Olefins are highly susceptible to atmospheric oxygen and can slowly oxidize to form stable radicals. These radicals initiate free-radical chain reactions, ultimately causing gum and sediment formation as well as changes in the physicochemical properties of a fuel [57]. Previous studies have shown that cyclic and conjugated olefins are the primary contributors to gum formation, whereas terminal and non-conjugated olefins play little to no role [58,59]. Branched olefins also contribute to gum deposits, although their reactivity depends on the position of branching. Consequently, by reducing the olefin content in WTPO, the hydrotreating process improves fuel quality and significantly enhances oxidation stability during storage.

Based on these observations, the olefinic region in the ¹H NMR spectra is divided into six zones (Table S1). These zones correspond to the following proton environments: olefinic CH₂ = protons of substituted α-olefins (O1, 4.50–4.80 ppm), CH₂ = protons of linear α-olefins (O2, 4.80–5.05 ppm), CH = protons of internal substituted olefins (O3, 5.05–5.34 ppm), CH = protons of internal linear and cyclic unsaturated species (O4, 5.34–5.73 ppm), CH = protons of linear α-olefins (O5, 5.73–5.90 ppm), and conjugated olefinic protons (O6, 5.90–6.20 ppm) [60]. The relative abundance of each olefinic type was estimated from the integrated ¹H NMR peak areas and is summarized in Table 4.

Crude WTPO contains a high proportion of substituted α-olefinic protons (O1), internal substituted olefinic protons (O3), and cyclic unsubstituted protons (O4) (Table 4), confirming the predominant presence of limonene as indicated by the GC/MS results. In general, regardless of olefin type, HYD reactivity increases with higher temperature, longer reaction time, and a greater catalyst-to-oil ratio (Table 3). Temperature has a particularly strong influence on the hydrogenation of terminal and conjugated alkenes, as reflected by the pronounced decrease in signal intensities in the O1, O2, O5, and O6 regions. This trend is consistent with the findings of Xin et al. [61], who reported that terminal alkenes are more reactive than internal alkenes under comparable conditions. A similar pattern was observed for reaction time:

Table 4Relative abundance of olefinic types (%) from integrating ^1H NMR olefinic chemical shift regions for WTPO and upgraded products at varying reaction conditions.

	Terminal substituted (O1)	Terminal linear (O2)	Internal substituted (O3)	Internal/cyclic unsubstituted (O4)	Internal linear (O5)	Conjugated (O6)
WTPO	0.89	0.65	1.44	0.93	0.21	0.28
Temperature ($^{\circ}\text{C}$) (*)						
340 $^{\circ}\text{C}$	0.47	0.46	1.27	0.61	0.14	0.16
360 $^{\circ}\text{C}$	0.24	0.24	1.05	0.47	0.05	0.05
380 $^{\circ}\text{C}$	0.18	0.17	0.92	0.38	0.02	0.03
400 $^{\circ}\text{C}$	0.20	0.21	1.04	0.41	0.01	0.03
Reaction time (h) (**)						
0.5 h	0.27	0.33	1.23	0.48	0.09	0.21
1 h	0.24	0.24	1.05	0.47	0.05	0.05
2 h	0.22	0.21	0.98	0.40	0.04	0.05
4 h	0.14	0.20	1.00	0.19	0.01	0.06
Catalyst/WTPO ratio (wt./wt.) (***)						
1:75	0.11	0.19	0.70	0.22	0.03	0.07
2:75	0.06	0.16	0.57	0.19	0.04	0.08
4:75	0.05	0.10	0.28	0.14	0.05	0.08
8:75	0.04	0.06	0.17	0.08	0.02	0.03

(*): initial H_2 pressure 40 bar, without H_2 replenishment, catalyst-to-WTPO ratio 1:75, 1 h.(**): 360 $^{\circ}\text{C}$, initial H_2 pressure 40 bar, without H_2 replenishment, catalyst-to-WTPO ratio 1:75.(***): 360 $^{\circ}\text{C}$, with H_2 replenishment at 70 bar, 4 h.

conjugated olefins (O6) were the most HYD reactive, followed by terminal alkenes (O1 and O2), internal unsubstituted alkenes (O4), and finally internal substituted alkenes (O3). These variations in HYD activity are attributed to steric effects; increased substitution around the $\text{C}=\text{C}$ bond reduces accessibility to the catalyst surface and thereby lowers hydrogenation reactivity [62].

In the final series examining catalyst loading, the periodic replenishment of hydrogen further enhanced HYD activity. At high catalyst loadings, olefin saturation became effective even for internal alkenes (O3 and O4). This outcome is consistent with previous studies [54,63], which reported that a greater number of Ni—Mo active sites alleviates a steric constraints associated with branching in internal and terminal substituted alkenes, thereby enhancing their saturation degree. Overall, operating conditions directly govern HYD performance; under conditions that favor efficient hydrogenation and olefin saturation, the resulting improvement in olefin stability can significantly influence the overall stability of the oils.

The liquid products were stored in sealed bottles for 60 days, and photographs of three representative samples are shown in Fig. 7. Fig. 7a

displays the oil obtained from the thermal cracking experiment conducted without catalyst, at an initial pressure of 40 bar Ar and 360 $^{\circ}\text{C}$ for 4 h, Fig. 7b shows the product from hydrocracking performed at an initial pressure of 40 bar H_2 (at room temperature), with a catalyst-to-oil of 1:75 at 360 $^{\circ}\text{C}$ for 4 h. Finally Fig. 7c presents the upgraded oil produced under conditions with periodic H_2 replenishment to 70 bar, using a catalyst-to-oil ratio of 8:75 at 360 $^{\circ}\text{C}$ for 4 h. Clear sediments (gum) deposits are visible along the walls of the bottle containing the thermally cracked oil (Fig. 7a), while substantially fewer deposits were observed in the hydrocracked sample (Fig. 7b). Notably, the liquid product from the experiment with H_2 replenishment showed excellent stability, with no visible gum deposits on the container walls after 60 days (Fig. 7c). These observations highlight the critical role of hydrogen availability and hydrogenation reactions in WTPO upgrading, resulting in significant improvements in product stability and overall fuel quality. Rahimi et al. [64] confirmed the beneficial impact of hydrotreatment on the storage stability of naphtha, jet and gas oil fractions from residue hydrocracking. Olefinic species, key precursors to gum formation and major contributor to fuel instability, are effectively stabilized during hydrotreatment.

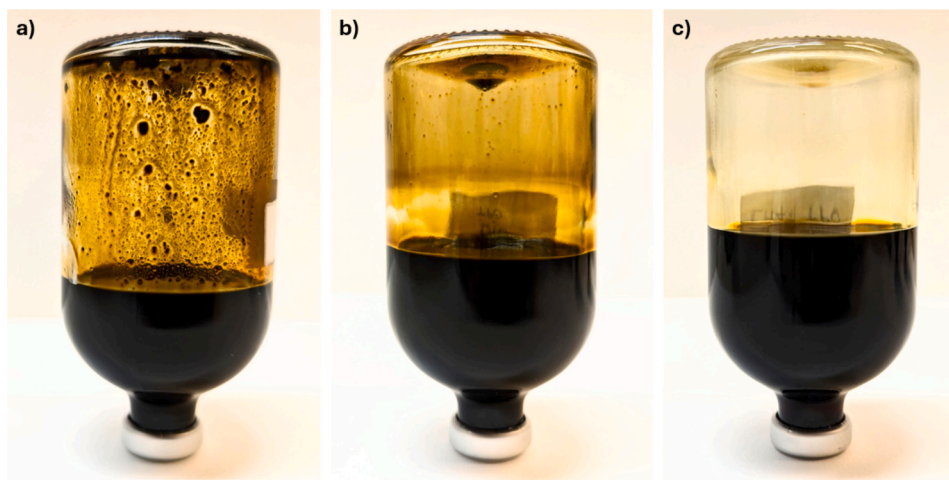


Fig. 7. Gums and sediments observed after 60 days of storage at room temperature: (a) Thermal cracking (360 $^{\circ}\text{C}$, 75 g of WTPO, 4 h, no catalyst, initial 40 bar Ar); (b) Hydrotreating without hydrogen replenishment (360 $^{\circ}\text{C}$, 75 g WTPO, 4 h, catalyst-to-oil ratio 1:75, initial 40 bar H_2 , no H_2 replenishment); (c) Hydrotreating with hydrogen replenishment (360 $^{\circ}\text{C}$, 75 g WTPO, 4 h, catalyst-to-oil ratio 8:75, initial 40 bar H_2 , with H_2 replenishment).

Processing at 360 °C for 4 h, and an elevated catalyst-to-oil ratio of 8:75, led to a progressive reduction in olefin content, particularly conjugated and internal cyclic olefins (Table 4). This reduction also clearly prevented gum and sediment formation in the corresponding hydrotreated oils during storage (Fig. 7b and c). These findings indicate that achieving high fuel stability requires minimizing the concentration of gum-forming olefins, which is in line with the observations reported by Pereira et al. [58].

3.4. Heteroatom removal efficiency and hydrogen consumption of WTPO hydrotreating

3.4.1. Sulfur removal efficiency and hydrogen uptake during WTPO hydrotreating

Among the heteroatoms present in WTPO, sulfur is the most abundant impurity, posing significant environmental concerns and directly affecting product quality. It is therefore critical to remove sulfur efficiently. The influence of operating parameters on sulfur removal was investigated, and the results are summarized in Fig. 8. Temperature had a pronounced effect on heteroatom removal (Fig. 8a). At lower temperatures (340–380 °C), HDS performance gradually improved,

reaching 14.7% at 380 °C. Increasing the temperature to 400 °C led to a dramatic rise in sulfur removal, achieving 28.1%. Since the sulfur compounds present in WTPO span various structural classes, they require different temperatures for effective removal. According to Zhang et al. [29], these compounds can be broadly categorized into five groups: thiophenes, benzothiophenes, dibenzothiophenes, substituted dibenzothiophenes, and non-aromatic sulfides. The reactivity of these species in HDS depends not only on operating temperature but also on their molecular structure [65]. Aliphatic sulfur species – such as sulfides, disulfides, mercaptans, and thiols – are highly reactive and can be readily desulfurized under mild conditions, typically below 180 °C [49]. In contrast, sulfur compounds with fused aromatic rings and alkyl substituents exhibit much lower reactivity [65]. This reduced reactivity arises from the participation of the sulfur atom's lone pair electrons in the conjugated C=C system of the aromatic rings, creating resonance stabilization and forming highly stable structures [49]. Under identical upgrading conditions, the relative HDS reactivity follows the order: thiophenes > benzothiophenes > dibenzothiophenes > alkyl-substituted dibenzothiophenes [29]. Robinson et al. [66] further reported that substituted dibenzothiophenes can be 100–150 times less reactive than other sulfur species and require significantly more severe

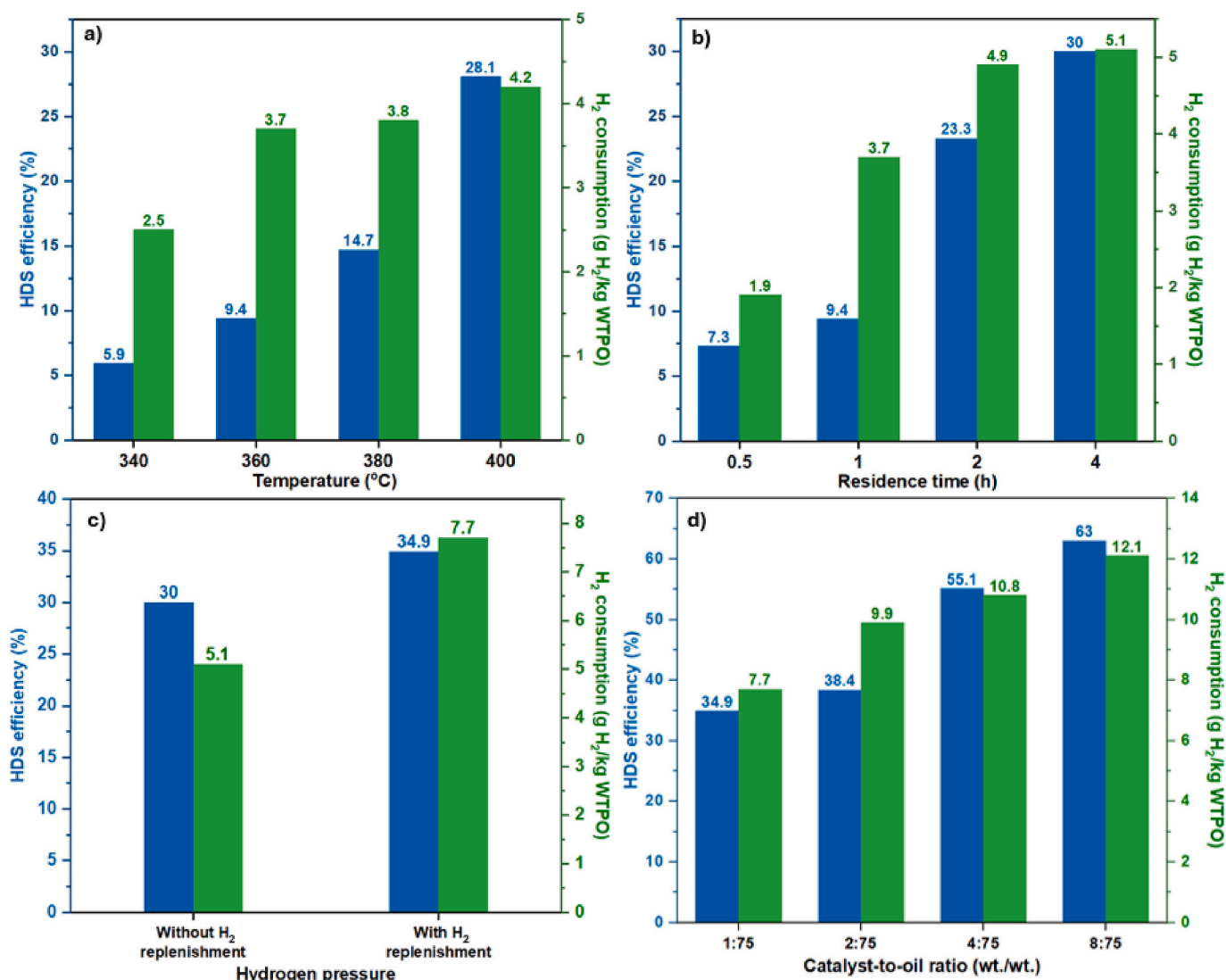


Fig. 8. HDS efficiency and hydrogen consumption of WTPO upgrading at (a) different reaction temperatures (initial H₂ pressure 40 bar, 75 g WTPO, catalyst-to-WTPO ratio 1:75, 1 h), (b) reaction times (360 °C, initial H₂ pressure 40 bar, 75 g WTPO, catalyst-to-WTPO ratio 1:75), (c) hydrogen pressure (360 °C, initial H₂ pressure 40 bar, 75 g WTPO, catalyst-to-WTPO ratio 1:75, 4 h), and (d) catalyst-to-WTPO ratio (360 °C, initial H₂ pressure 40 bar with H₂ replenishment every 15 min, 75 g WTPO, 4 h).

desulfurization conditions, typically above 380 °C.

Besides, hydrogen consumption increased with rising temperature, and the hydrogen content of the upgraded oil reached 11.3 wt% at 360 °C, compared to 10.9 wt% in the WTPO feedstock (Table S2). However, hydrogen consumption did not increase significantly at temperatures above 360 °C (Fig. 8a). This behavior may be attributed to a progressive shift in the dominant reaction pathway — from hydrogenation to thermal cracking — which competes with HYD. Consequently, only a modest increase in hydrogen consumption was observed when the temperature was raised to 400 °C. This trend aligns with the findings of Dimitrisdis et al. [67], who reported that elevated reaction temperatures strongly promote cracking reactions.

Fig. 8b illustrates the effect of reaction time on H₂ consumption and HDS efficiency during WTPO upgrading at 360 °C. Consistent with the fraction-distribution and compositional trends shown in Fig. 4, HDS efficiency increased slightly during the first hour, driven by active hydrogenation. This strong hydrogenation activity is reflected in the rise in hydrogen consumption from 1.9 g H₂/ kg WTPO to 3.7 g H₂/ kg WTPO. At longer reaction times, HDS efficiency improved further, reaching 23.3% and eventually 30% after 4 h. These results indicate that HYD plays a critical role in sulfur removal, typically preceding and facilitating the HDS process. The time-dependent improvement in sulfur removal may be attributed, at least in part, to the transformation of catalyst active phases during upgrading. At the early stage of the reaction, the catalyst likely consisted of reduced metal sites derived from the initial metal oxides or intermediate reduced states (Ni, MoO₂). These metal sites were progressively sulfided by H₂S generated from sulfur-bearing species in WTPO, forming sulfided phases such as Ni₃S₂ and MoS₂, which are known to exhibit favorable HYD and HDS activity [4]. The gradual formation of these sulfided phases promotes hydrogenation of sulfur-containing species and increases hydrogen uptake, thereby enhancing HDS activity with increasing reaction time. In addition, extended reaction time increases the contact between sulfur species and catalytic sites, further promoting hydrotreating reactions. However, hydrogen consumption increased only slightly after 2 h, accompanied by a slower rise in HDS efficiency. This behavior can possibly be attributed to the significant decline in hydrogen pressure over time, which limits both HYD and HDS activities. These results align with the findings of Bello et al. [68], who reported hydrogen insufficiency can hinder HDS performance.

On the other hand, Fig. 8c compares hydrogen consumption and HDS performance for experiments conducted with and without H₂ replenishment. Hydrogen consumption increased markedly when hydrogen

was periodically replenished, whereas HDS efficiency — largely driven by cracking — showed only a modest improvement, highlighting the competitive relationship between hydrogenation and cracking discussed earlier. This further confirms the competition between HYD and cracking pathways. Fig. 8d shows the influence of the catalyst-to-oil ratio. Hydrogen consumption increased proportionally with the catalyst/WTPO ratio, rising from 7.7 to 12.1 g H₂/kg WTPO. Higher catalyst loadings provide more active sites, thereby enhancing HYD activity. This trend is consistent with the chemical composition changes shown in Fig. 6b, where increased olefin saturation corresponds to higher levels of aliphatics and monocycloalkanes. The higher hydrogen uptake at elevated catalyst loadings likely facilitates hydrogenation of more refractory sulfur species, contributing to the improved heteroatom removal observed in these experiments.

Analyzing individual sulfur-containing compounds in WTPO by GC-MS is challenging due to their low concentrations and overlap with hydrocarbon peaks. To gain deeper insight into the transformation of different sulfur species and to minimize interference from hydrocarbons, GC-SCD was employed to monitor sulfur compounds during hydrotreating. Both the fresh WTPO and the hydrotreated product obtained at 360 °C and 70 bar, using a catalyst-to-oil ratio of 8:75 (g/g) for 4 h, were analyzed using GC-SCD. The resulting chromatograms for both samples, along with standards of representative sulfur compounds, are presented in Fig. 9.

Three major peaks appear in the standard sample at retention times of 6.9, 18.0, and 26.4 min, corresponding to thiophene, benzothiophene, and dibenzothiophene, respectively. Because of the highly complex composition of WTPO, assigning specific chemical structures to each individual chromatographic peak was not feasible. Instead, the peaks were grouped into four categories based on retention times and the reference compounds: an aliphatic group (< 6.9 min), a thiophene group (one ring, 6.9–18.0 min), a benzothiophene group (two rings, 18–26.4 min), and a bulky group (three or more rings, > 26.4 min). Benzothiazole and its derivatives were identified as the most abundant sulfur species in fresh WTPO, originating from the thermal cracking of vulcanization accelerators [31]. Additional peaks corresponding to mercaptans, methylthiophenes, benzothiophenes and their methyl-substituted derivatives, as well as dibenzothiophenes, were also detected.

To enable a clearer comparison between the oil before and after hydrotreating (HDT), a quantitative assessment was performed based on the total peak areas of each compound group, as presented in Fig. 10 and Table S3. Organosulfur compounds lacking aromatic structures were effectively eliminated. In contrast, aromatic sulfur species exhibited

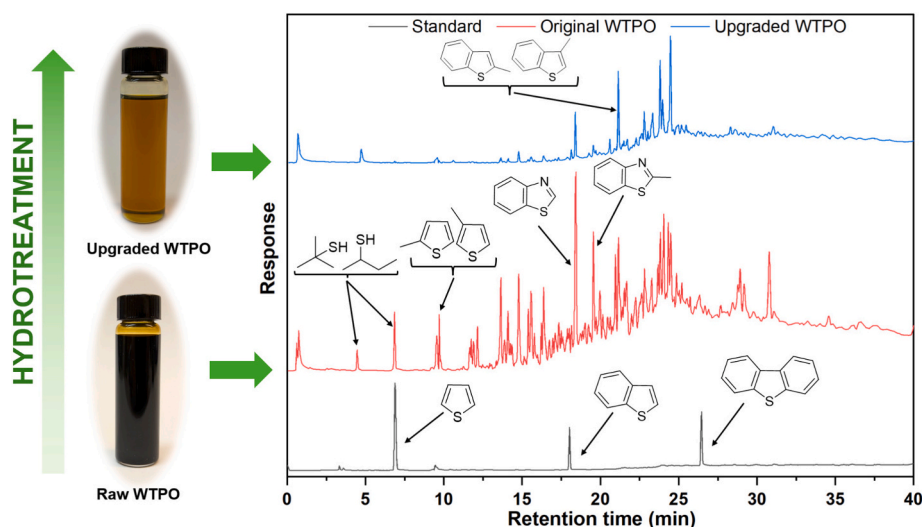


Fig. 9. Appearance and corresponding GC-SCD chromatographs of WTPO and its upgraded product over NiMo/Al₂O₃ catalyst (with 63% sulfur removal). Reaction conditions: 360 °C, hydrogen replenishment to 70 bar every 15 min, with catalyst-to-oil ratio 8:75, for 4 h.

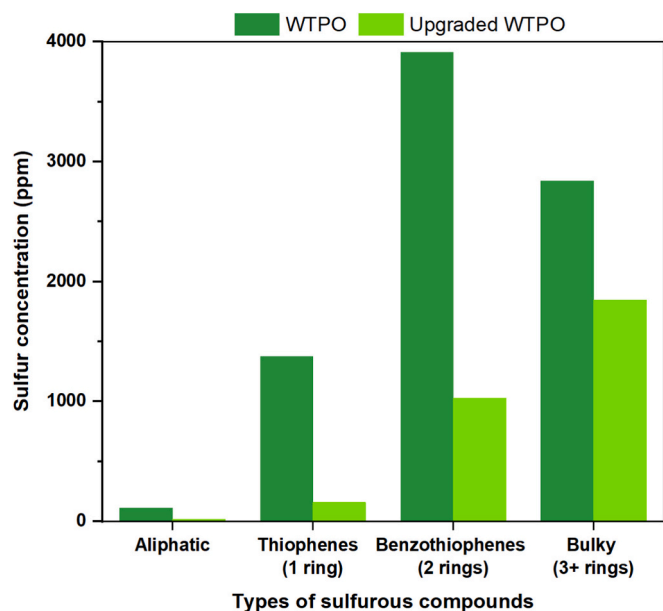


Fig. 10. Sulfurous compound distribution in WTPO and hydrotreated product (with 63% sulfur removal). Reaction conditions: 360 °C, hydrogen replenishment to 70 bar every 15 min, catalyst-to-oil ratio 8:75 (g/g), 4 h.

lower HDS reactivity, with molecular structure emerging as the key determining factor. Specifically, thiophenes and their derivatives demonstrated high reactivity, achieving an HDS efficiency of 88.5%. By comparison, compounds with more complex and highly aromatic structures – such as those containing two fused rings – displayed greater resistance to desulfurization, resulting in lower removal efficiencies [69]. Bulky sulfur-bearing compounds with three or more fused rings remained the most abundant group in the upgraded products, indicating that they possess the lowest HDS reactivity.

3.4.2. Effects of operating parameters on the removal of other heteroelements

In addition to sulfur, the nitrogen and oxygen contents of oils are also crucial factors in refining processes and in determining final fuel quality. Higher oxygen concentration often corresponds to higher fuel acidity, which can cause corrosion in processing equipment and pipelines [39]. Meanwhile, nitrogen compounds contribute to greenhouse gas emissions during fuel combustion, resulting in many environmental concerns [70]. In addition, nitrogen species can also promote catalyst deactivation [71]. In general, nitrogen compounds are more resistant to hydrotreating than oxygen- and sulfur-containing compounds. Due to their highly stable structures, nitrogen removal typically requires harsher operating conditions [72]. The denitrogenation pathway involves initial hydrogenation of the nitrogen-bearing ring, followed by ring opening caused by C–N bond cleavage and subsequent hydrogenolysis, ultimately producing ammonia and the corresponding hydrocarbon [73].

The heteroatom-removal efficiencies under various operating conditions are presented in Table S2. Temperature exerted a strong proportional influence on heteroatom removal. At a fixed operating temperature of 360 °C, the removal of nitrogen and oxygen increased progressively with reaction time, reaching maximum HDN and HDO efficiency values of 33.9% and 47.4%, respectively, after 4 h. Notably, under similar reaction conditions, periodically replenishing hydrogen led to a dramatic increase in both HDN and HDO efficiencies, raising them to 44.1% and 53.9%, respectively. A comparable enhancement was observed when the number of catalyst active sites increased. At the highest catalyst loading of 8:75 (wt./wt.), HDN reached 67.8%, while HDO increased to 65.8%. Since the hydrogen replenishment and the number of active sites directly influence HYD activity, these results

emphasize the central role of HYD in WTPO hydrotreating.

3.5. Catalyst regeneration evaluation

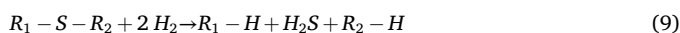
Catalyst deactivation is a major concern in petroleum refineries, as it leads to costly process shutdowns and frequent catalyst replacement. The loss of catalytic activity is influenced by various factors, including feedstock composition, catalyst formulation, and operating conditions [71]. Based on the results presented in previous sections, a series of reusability experiments were conducted during WTPO upgrading under the following conditions: 360 °C, H₂ periodically replenished to 70 bar (360 °C), 75 g of WTPO, catalyst-to-oil ratio of 8:75 (wt./wt.) and a reaction time of 4 h. After each run, the spent catalyst was recovered and washed three times with 10 mL of acetone to remove residual organics, then dried overnight at 80 °C. The regenerated catalyst was subsequently calcined in air at 450 °C for 6 h, reduced at 450 °C under an initial hydrogen pressure of 20 bar for 5 h, and finally passivated using 2.0% O₂ in argon before reuse in the next reaction cycle. This temperature was selected since regeneration by air-calcination is typically performed within the range of 400 to 550 °C. Dufresne et al. [74] reported that this temperature window enables removal of carbonaceous species while minimizing the risk of metal sintering or structural changes.

Fig. 11 illustrates the catalytic performance over three consecutive reaction cycles. In general, the reaction remained stable, yielding approximately 97% liquid product (with ca. 3% gas and no solid formation), producing a consistent middle-distillate fraction of 54–55 wt% in each cycle. The GC detectable yield increased from 76.3 wt% in the first run to 79.0 wt% in the third run, accompanied by a rise in aliphatic content from 23.5 wt% to 27.0 wt%. The regenerated catalyst exhibited upgrading performance comparable to that obtained in three replicate experiments performed under identical conditions using fresh catalyst (Table S4). These results indicate that no significant deactivation occurred after regeneration, demonstrating that air-combustion effectively restored the catalytic activity.

Moreover, according to Fig. 11c, HDS efficiency also improved slightly, along with a minor increase in hydrogen consumption, suggesting a modest enhancement in cracking activity. This observation is in line with a study by Kohli et al. [75] on heavy oil hydroprocessing, demonstrating that the activity of a regenerated NiMo/Al₂O₃ catalyst was fully restored by air-calcination. Moreover, elemental analysis (Table S5) indicated that the C, H, N, and O contents of the hydrotreated oil remained nearly unchanged across all cycles. Together, these results demonstrate that WTPO hydrotreating under the tested conditions enables effective heteroatom removal while maintaining catalyst stability, with minimal deactivation observed after each regeneration step involving calcination in air at 450 °C for 6 h.

3.6. Sulfur removal mechanism in WTPO hydrotreating

To contextualize the heteroatom removal achieved during WTPO hydrotreating, the experimental results were compared with HDS pathways previously reported in the literature. GC-SCD analysis in Fig. 10 indicated that the ease of sulfur removal followed the order: aliphatic organosulfur > thiophenes > benzothiazoles ≈ benzothiophenes > dibenzothiophenes. These classes of sulfur compounds undergo distinct HDS pathways, as illustrated in Scheme 1. Specifically, aliphatic organosulfur molecules, which are highly reactive, are readily removed through hydrodesulfurization [65,76]. Their conversion (Eqs. 8–10), leads to a pronounced decrease in the corresponding peak intensities in the GC-SCD chromatograms of the hydrotreated oil, as shown in Fig. 9.



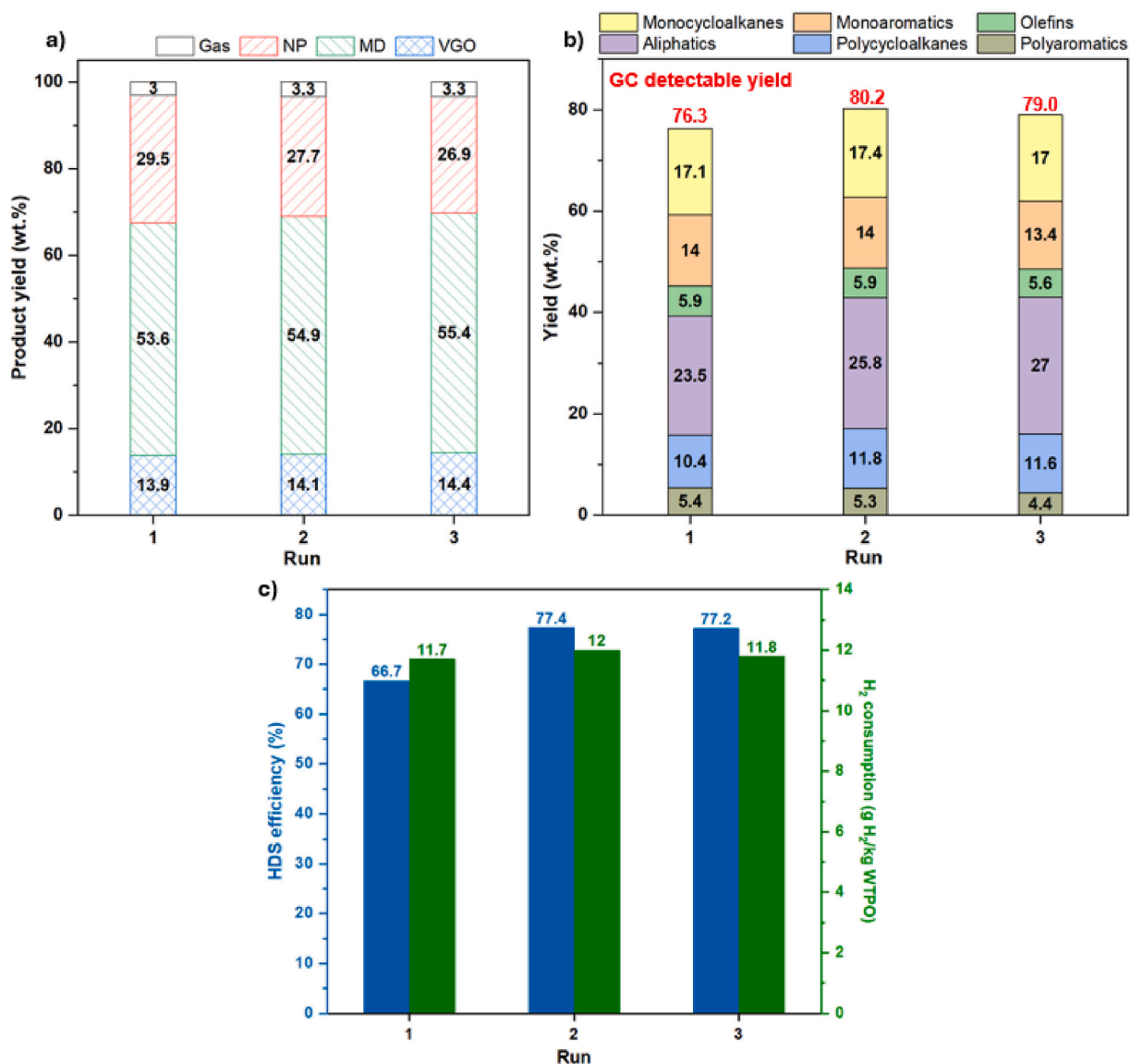
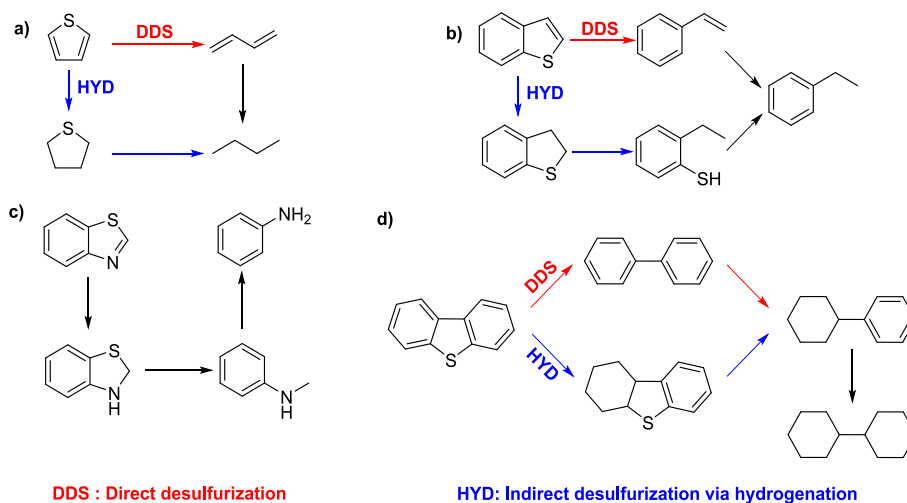
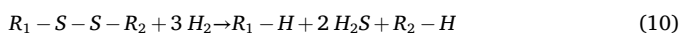


Fig. 11. Regeneration performance of NiMo/Al₂O₃ during WTPO hydrotreating: (a) product distribution from TGA, (b) liquid-phase chemical composition, and (c) HDS efficiency and H₂ consumption. Reaction conditions: 360 °C, periodic H₂ replenishment to 70 bar, 75 g WTPO, catalyst-to-WTPO ratio 8:75, 4 h.



Scheme 1. An overview on the removal of typical sulfur-containing compounds present in WTPO during hydrotreating.



where R, R₁, and R₂ represent alkyl groups.

For heterocyclic sulfur-containing compounds, two main desulfurization pathways are generally recognized: direct desulfurization (DDS) and indirect desulfurization via prior hydrogenation (HYD) [3]. Thiophene derivatives, owing to their relatively simple structures, are removed predominantly through the DDS pathway (Scheme 1a), in which the C—S bond is cleaved to form H₂S and alkenes; these alkenes may subsequently undergo hydrogenation to form alkanes [77]. In contrast, benzothiophene-based molecules, which contain a fused benzene ring, undergo both DDS and HYD routes (Scheme 1b). Benzothiazoles preferentially undergo C—S bond cleavage to form the corresponding aniline derivatives; however, further denitrogenation of anilines to hydrocarbons is challenging because of the high basicity and stability of the intermediate. This observation is consistent with previous studies [78,79], reporting that aniline is a persistent HDS intermediate during the transformation of benzothiazoles (Scheme 1c).

On the other hand, the removal of dibenzothiophenes, their alkyl-substituted derivatives and polyaromatic sulfurous compounds (see Scheme 1d) is even more difficult and requires an effective combination of hydrogenation and cracking steps. The refractory nature of these species is likely reflected in the moderate removal of bulky sulfurous substrates, as illustrated in Fig. 10. Although both DDS and HYD pathways contribute to their desulfurization, DDS is generally the favored pathway for unsubstituted dibenzothiophenes [80]. However, the presence of alkyl substituents adjacent to the sulfur atom introduces significant steric hindrance, which lowers the ability of these species to reach catalytically active sites and suppresses the DDS route more strongly than the HYD route [81]. As a result, desulfurization of these refractory species likely proceeds predominantly through hydrogenation followed by C—S bond cleavage. This interpretation is supported by the pronounced enhancement in overall sulfur removal observed with hydrogen replenishment and increased catalyst loading, as shown in Fig. 8.

4. Conclusions

In summary, we systematically investigated the hydrotreating of WTPO under a range of operating conditions, highlighting the competing influences of hydrogenation and cracking pathways. The evolution of WTPO fractions and representative compound groups was examined in detail. At lower temperatures hydrogenation was effective, whereas at 380 and 400 °C the cracking increased. In the absence of hydrogen (i.e., under an Ar atmosphere), WTPO upgrading suffered from lower conversion and undesirable gas formation. Hydrogen plays an important role in weakening unsaturated C=C bonds and heterocyclic structures. Without sufficient hydrogenation, polyaromatic compounds remain largely inert, resulting in poor carbon utilization.

Under hydrogenation-favorable conditions – specifically with periodic hydrogen replenishment and an increased catalyst-to-oil ratio of 8:75 – an HDS efficiency of 63.0% was achieved. These conditions also promoted substantial conversion of heavy fractions into lighter products, as reflected by a GC-MS detectable liquid yield of 75.9 wt%. Notably, most unstable olefins were fully saturated, yielding a higher-quality fuel even at the relatively mild temperature of 360 °C. This effective upgrading performance suppresses the formation of gums and sediments, thereby improving the storage stability of the upgraded oil. The process achieved a total liquid yield of 96.7%, consisting of 28.2 wt % naphtha and 54.2 wt% middle distillate – both valuable liquid fuel components. According to GC-SCD analysis, small sulfur-bearing compounds were effectively removed, whereas polyaromatic sulfur compounds are more difficult to eliminate via hydrotreatment. Furthermore, these operating conditions enabled multiple reaction cycles with minimal catalyst deactivation following re-calcination, maintaining stable

catalytic performance. Overall, this study establishes a strong foundation for renewable fuel production from waste-tire pyrolysis oil, providing practical chemical insights that support both catalyst design and process optimization.

Originality statement

This manuscript is original, has not been published previously, and is not under consideration for publication elsewhere.

CRediT authorship contribution statement

Huy Xuan Le: Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **Tung Manh Nguyen:** Writing – review & editing, Validation, Supervision, Conceptualization. **Emma Rehn:** Methodology. **Phuoc Hoang Ho:** Validation, Methodology. **Quoc Khanh Tran:** Validation, Methodology. **Olov Öhrman:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization. **Derek Creaser:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Louise Olsson:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Conceptualization.

Author approval

All authors have read and approved the final manuscript and agree to its submission to Fuel Processing Technology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This work has been performed at the Competence Centre for Catalysis (KCK) and the Chemical Engineering division at the Chalmers University of Technology in collaboration with VAROPreem. The Competence Centre for Catalysis is hosted by Chalmers University of Technology and financially supported by the Swedish Energy Agency (Project No. 52689-1) and the member companies Johnson Matthey, Perstorp, PowerCell Sweden, TRATON, Umicore, VAROPreem and Volvo Group. KCK is gratefully acknowledged for the financial support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuproc.2026.108607>.

Data availability

Data will be made available on request.

References

- [1] E.T.R.M. Association, First quarter replacement sales: consumer tyre growth continues. <https://www.etrma.org/news/first-quarter-replacement-sales-consumer-tyre-growth-continues/>, 2025 (Accessed 08 May 2025).
- [2] M.M. Rahman, Y. Yu, H. Wu, Valorisation of waste tyre via pyrolysis: advances and perspectives, *Energy Fuel* 36 (20) (2022) 12429–12474, <https://doi.org/10.1021/acs.energyfuels.2c02053>.
- [3] G. Zhang, F. Chen, Y. Zhang, L. Zhao, J. Chen, L. Cao, J. Gao, C. Xu, Properties and utilization of waste tire pyrolysis oil: a mini review, *Fuel Process. Technol.* 211 (2021) 106582, <https://doi.org/10.1016/j.fuproc.2020.106582>.
- [4] Q. Zhang, I. Jones, M. Zhu, Z. Zhang, J. Gao, D. Zhang, Catalytic hydrodesulfurization of a spent tire pyrolysis oil distillate over a Ni–Mo catalyst, *Ind. Eng. Chem. Res.* 61 (4) (2022) 1624–1635, <https://doi.org/10.1021/acs.iecr.1c03240>.

- [5] M. Hashamifirooz, M.H. Dehghani, M. Khanizadeh, M. Aghaei, P. Bashardoost, M. S. Hassanvand, M. Hassanabadi, F. Momeni, A systematic review of the environmental and health effects of waste tires recycling, *Heliyon* 11 (2) (2025) e41909, <https://doi.org/10.1016/j.heliyon.2025.e41909>.
- [6] X. Liu, Z. Li, X. Gou, Advances and outlook on desulfurization and utilization of tire pyrolysis oil: a review, *Energy Fuel* 38 (22) (2024) 21889–21912, <https://doi.org/10.1021/acs.energyfuels.4c04244>.
- [7] M. Arabiourrutia, G. Lopez, M. Artetxe, J. Alvarez, J. Bilbao, M. Olazar, Waste Tyre valorization by catalytic pyrolysis – a review, *Renew. Sust. Energ. Rev.* 129 (2020) 109932, <https://doi.org/10.1016/j.rser.2020.109932>.
- [8] Y. Hu, M. Attia, E. Tabet, A. Mohaddespour, M.T. Munir, S. Farag, Valorization of waste tire by pyrolysis and hydrothermal liquefaction: a mini-review, *J. Mater. Cycles Waste Manag.* 23 (5) (2021) 1737–1750, <https://doi.org/10.1007/s10163-021-01252-1>.
- [9] N. Bergvall, Y.W. Cheah, C. Bernlind, A. Bernlind, L. Olsson, D. Creaser, L. Strandström, O.G.W. Öhrman, Upgrading of fast pyrolysis bio-oils to renewable hydrocarbons using slurry- and fixed bed hydroprocessing, *Fuel Process. Technol.* 253 (2024) 108009, <https://doi.org/10.1016/j.fuproc.2023.108009>.
- [10] P. Tamizhdurai, P. Arthi, V.L. Mangesh, P.S. Krishnan, N.S. Kumar, P. Saravanan, A. Subramani, P. Sasikumar, M.F. Alotibi, S.B. Alreshaidan, A.A.M. Abahussain, S. Al-Fateh, R. Kumaran, Clean energy technology: hydro-processing of waste tyre pyrolysis oil (WTPO) to diesel fuel in a continuous reactor using Co/SBA-15 catalyst, *Appl. Energy Combust. Sci.* 21 (2025) 100305, <https://doi.org/10.1016/j.jaecs.2024.100305>.
- [11] F. Campuzano, A.G. Abdul Jameel, W. Zhang, A.-H. Emwas, A.F. Agudelo, J. D. Martínez, S.M. Sarathy, Fuel and chemical properties of waste tire pyrolysis oil derived from a continuous twin-auger reactor, *Energy Fuel* 34 (10) (2020) 12688–12702, <https://doi.org/10.1021/acs.energyfuels.0c02271>.
- [12] F. Campuzano, A.G. Abdul Jameel, W. Zhang, A.-H. Emwas, A.F. Agudelo, J. D. Martínez, S.M. Sarathy, On the distillation of waste tire pyrolysis oil: a structural characterization of the derived fractions, *Fuel* 290 (2021) 120041, <https://doi.org/10.1016/j.fuel.2020.120041>.
- [13] S. Cañete, L. Faba, S. Ordóñez, Continuous hydrogenation of plastic wastes pyrolysis oil over used hydrotreatment catalysts, *Catal. Today* 454 (2025) 115308, <https://doi.org/10.1016/j.cattod.2025.115308>.
- [14] F. Campuzano, J.D. Martínez, A.F. Agudelo Santamaría, S.M. Sarathy, W. L. Roberts, Pursuing the end-of-life tire circularity: an outlook toward the production of secondary raw materials from tire pyrolysis oil, *Energy Fuel* 37 (13) (2023) 8836–8866, <https://doi.org/10.1021/acs.energyfuels.3c00847>.
- [15] R. Idris, W.W.F. Chong, J.-H. Ng, W.A.W. Mahari, S.S. Lam, G.R. Mong, A. Ali, S. Idris, R. Roslee, N. Surugau, B.B. Nyakuma, A review on non-catalytic and catalytic co-pyrolysis of waste tire and biomass for upgrading pyrolysis oil, *Renew. Sust. Energ. Rev.* 239 (2026) 117117, <https://doi.org/10.1016/j.rser.2026.117117>.
- [16] N. Jantaraksa, P. Prasassarakich, P. Reubroycharoen, N. Hinchiranan, Cleaner alternative liquid fuels derived from the hydrodesulfurization of waste tire pyrolysis oil, *Energy Convers. Manag.* 95 (2015) 424–434, <https://doi.org/10.1016/j.enconman.2015.02.003>.
- [17] S. Kingputtpong, N. Chanlek, Y. Poo-arporn, N. Hinchiranan, Production of cleaner waste tire pyrolysis oil by removal of polycyclic aromatic hydrocarbons via hydrogenation over Ni-based catalysts, *Int. J. Energy Res.* 46 (11) (2022) 16082–16101, <https://doi.org/10.1002/er.8290>.
- [18] Y. Han, F. Stankovikj, M. Garcia-Perez, Co-hydrotreatment of tire pyrolysis oil and vegetable oil for the production of transportation fuels, *Fuel Process. Technol.* 159 (2017) 328–339, <https://doi.org/10.1016/j.fuproc.2017.01.048>.
- [19] R. Palos, T. Kekäläinen, F. Duodu, A. Gutiérrez, J.M. Arandes, J. Jänis, P. Castaño, Screening hydrotreating catalysts for the valorization of a light cycle oil/scrap tires oil blend based on a detailed product analysis, *Appl. Catal. B Environ.* 256 (2019) 117863, <https://doi.org/10.1016/j.apcatb.2019.117863>.
- [20] R. Palos, T. Kekäläinen, F. Duodu, A. Gutiérrez, J.M. Arandes, J. Jänis, P. Castaño, Detailed nature of tire pyrolysis oil blended with light cycle oil and its hydroprocessed products using a NiW/HY catalyst, *Waste Manag.* 128 (2021) 36–44, <https://doi.org/10.1016/j.wasman.2021.04.041>.
- [21] X.-J. Liu, F. Wang, L.-L. Zhai, Y.-P. Xu, L.-F. Xie, P.-G. Duan, Hydrotreating a waste engine oil and scrap tire oil blend for production of liquid fuel, *Fuel* 249 (2019) 418–426, <https://doi.org/10.1016/j.fuel.2019.03.129>.
- [22] O.S. Djandja, Z. Wang, P. Duan, F. Wang, Y. Xu, Hydrotreatment of pyrolysis oil from waste tire in tetralin for production of high-quality hydrocarbon rich fuel, *Fuel* 285 (2021) 119185, <https://doi.org/10.1016/j.fuel.2020.119185>.
- [23] Y. Zhang, F. Liu, W. Chen, W. Han, W. Zhai, Y. Lu, M. Li, Effective reduction of hydrogen consumption in ultra-deep hydrodesulfurization of diesel: deep insights into the effect of thermodynamic limitations during hydrotreating, *Fuel* 356 (2024) 129640, <https://doi.org/10.1016/j.fuel.2023.129640>.
- [24] E. Nejadmoghadam, A. Achour, O. Öhrman, M.A. Salam, D. Creaser, L. Olsson, Stabilization of fresh and aged simulated pyrolysis oil through mild hydrotreatment using noble metal catalysts, *Energy Convers. Manag.* 313 (2024) 118570, <https://doi.org/10.1016/j.enconman.2024.118570>.
- [25] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodríguez-Reinoso, J. Rouquerol, K.S.W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), *Pure Appl. Chem.* 87 (9–10) (2015) 1051–1069, <https://doi.org/10.1515/pac-2014-1117>.
- [26] Y. Zhang, Y. Wang, H. Cui, F. Wang, Z. Li, C. Sun, Y. Jia, Y. Xie, F. Song, J. Wang, W. Yi, Co-pyrolysis of biomass with Red Mud: an efficient approach to improving bio-oil quality and resourceful utilization of the iron in Red Mud, *Fuel* 355 (2024) 129482, <https://doi.org/10.1016/j.fuel.2023.129482>.
- [27] L. Wang, X. Wang, J. Yu, A comparative study of the pyrolysis and hydrolysis conversion of tire, *J. Hazard. Mater.* 468 (2024) 133724, <https://doi.org/10.1016/j.jhazmat.2024.133724>.
- [28] J. Alvarez, G. Lopez, M. Amutio, N.M. Mkhize, B. Danon, P. van der Grypt, J. F. Görgens, J. Bilbao, M. Olazar, Evaluation of the properties of Tyre pyrolysis oils obtained in a conical spouted bed reactor, *Energy* 128 (2017) 463–474, <https://doi.org/10.1016/j.energy.2017.03.163>.
- [29] X. Zhang, J. Tang, J. Chen, Behavior of sulfur during pyrolysis of waste tires: a critical review, *J. Energy Inst.* 102 (2022) 302–314, <https://doi.org/10.1016/j.joei.2022.04.006>.
- [30] M.S. Abbas-Abadi, M. Kusenberger, H.M. Shirazi, B. Goshayeshi, K.M. Van Geem, Towards full recyclability of end-of-life tires: challenges and opportunities, *J. Clean. Prod.* 374 (2022) 134036, <https://doi.org/10.1016/j.jclepro.2022.134036>.
- [31] Y. Zhang, S. Li, Q. Zhang, Y. Zhao, M. Liu, D. Zhang, X. Cai, N. Wang, W. Wang, Structural characterization and transformation of nitrogen compounds in waste tire pyrolysis oils, *J. Chromatogr. A* 1702 (2023) 464093, <https://doi.org/10.1016/j.chroma.2023.464093>.
- [32] S.A. Channiwala, P.P. Parikh, A unified correlation for estimating HHV of solid, liquid and gaseous fuels, *Fuel* 81 (8) (2002) 1051–1063, [https://doi.org/10.1016/S0016-2361\(01\)00131-4](https://doi.org/10.1016/S0016-2361(01)00131-4).
- [33] P. Straka, M. Auersvald, D. Vrtiška, H. Kittel, P. Šimáček, P. Vozka, Production of transportation fuels via hydrotreating of scrap tires pyrolysis oil, *Chem. Eng. J.* 460 (2023) 141764, <https://doi.org/10.1016/j.cej.2023.141764>.
- [34] Y. Wang, J. Lu, X. Zhang, X. Zhang, B. Zhang, J. Wu, D. Guan, Y. Zhang, J. Chen, X. Feng, Y. Zhang, Z. Zhou, L. Zhang, Q. Shi, Molecular transformation of heavy oil during slurry phase hydrocracking process: a comparison between thermal cracking and hydrocracking, *Fuel* 351 (2023) 128981, <https://doi.org/10.1016/j.fuel.2023.128981>.
- [35] I. Hita, A.T. Aguayo, M. Olazar, M.J. Azkoiti, J. Bilbao, J.M. Arandes, P. Castaño, Kinetic modeling of the hydrotreating and hydrocracking stages for upgrading scrap tires pyrolysis oil (STPO) toward high-quality fuels, *Energy Fuel* 29 (11) (2015) 7542–7553, <https://doi.org/10.1021/acs.energyfuels.5b01502>.
- [36] W. Tang, M. Fang, H. Wang, P. Yu, Q. Wang, Z. Luo, Mild hydrotreatment of low temperature coal tar distillate: product composition, *Chem. Eng. J.* 236 (2014) 529–537, <https://doi.org/10.1016/j.cej.2013.09.038>.
- [37] A.G. Abdul Jameel, N. Naser, G. Issayev, J. Toutiou, M.K. Ghosh, A.-H. Emwas, A. Farooq, S. Dooley, S.M. Sarathy, A minimalist functional group (MFG) approach for surrogate fuel formulation, *Combust. Flame* 192 (2018) 250–271, <https://doi.org/10.1016/j.combustflame.2018.01.036>.
- [38] N. Zhen, X.-D. Zhou, X.-L. Yin, J.-M. Liu, Y.-K. Tang, T. Liu, L. Liu, Different effect of H₂ and H-donating solvent on aromatic formation during the direct coal liquefaction of naomao coal, *Fuel* 397 (2025) 135416, <https://doi.org/10.1016/j.fuel.2025.135416>.
- [39] S. Badoga, A. Alvarez-Majmutov, J.K. Rodriguez, J. Chen, Upgrading of hydrothermal liquefaction biocrude from forest residues using solvents and mild hydrotreating for use as co-processing feed in a refinery, *Energy Fuel* 37 (17) (2023) 13104–13114, <https://doi.org/10.1021/acs.energyfuels.2c03747>.
- [40] B. Kunwar, S.D. Deilami, L.E. Macaskie, J. Wood, P. Biller, B.K. Sharma, Nanoparticles of Pd supported on bacterial biomass for hydroprocessing crude bio-oil, *Fuel* 209 (2017) 449–456, <https://doi.org/10.1016/j.fuel.2017.08.007>.
- [41] E. Heracleous, F. Papadopoulou, A.A. Lappas, Slurry-phase hydrotreating of vacuum gas oil with Mo-based dispersed catalyst in semi-batch and continuous reactors, *Fuel Process. Technol.* 276 (2025) 108271, <https://doi.org/10.1016/j.fuproc.2025.108271>.
- [42] C. Mateus-Rubiano, A.C. Castillo, P. León, L. Rueda, D. Molina, V.A. Leon, Effect of hydrotreatment process on the physicochemical properties of a Colombian heavy crude oil post-catalytic aquathermolysis, *Energy* 298 (2024) 131349, <https://doi.org/10.1016/j.energy.2024.131349>.
- [43] K. Kohansal, K. Sharma, M.S. Haider, S.S. Toor, D. Castello, L.A. Rosendahl, J. Zimmermann, T.H. Pedersen, Hydrotreating of bio-crude obtained from hydrothermal liquefaction of biopulp: effects of aqueous phase recirculation on the hydrotreated oil, *Sustainable Energy Fuels* 6 (11) (2022) 2805–2822, <https://doi.org/10.1039/D2SE00399F>.
- [44] Y. Feng, J. Deng, W. Lang, D. Chen, Z. Zhu, Z. Yang, K. Sun, X. Luo, S. Yuan, Efficient hydrotreatment of waste tire pyrolysis oil using N-doped biochar loaded with cobalt-molybdenum carbide, *J. Hazard. Mater.* 480 (2024) 136238, <https://doi.org/10.1016/j.jhazmat.2024.136238>.
- [45] M. Abdi-Khanghah, A. Jafari, G. Ahmadi, A. Hemmati-Sarapardeh, Optimization of reaction temperature and Ni–W–Mo catalyst soaking time in oil upgrading: application to kinetic modeling of in-situ upgrading, *Sci. Rep.* 13 (1) (2023) 6158, <https://doi.org/10.1038/s41598-023-31314-3>.
- [46] K.A. Gould, I.A. Wiehe, Natural Hydrogen Donors in Petroleum Resids, *Energy Fuel* 21 (3) (2007) 1199–1204, <https://doi.org/10.1021/ef060349t>.
- [47] Y. Miki, S. Yamadaya, M. Oba, Y. Sugimoto, Role of catalyst in hydrocracking of heavy oil, *J. Catal.* 83 (2) (1983) 371–383, [https://doi.org/10.1016/0021-9517\(83\)90062-3](https://doi.org/10.1016/0021-9517(83)90062-3).
- [48] H. Du, D. Liu, H. Liu, P. Gao, R. Lv, M. Li, B. Lou, Y. Yang, Role of hydrogen pressure in slurry-phase hydrocracking of venezuela heavy oil, *Energy Fuel* 29 (4) (2015) 2104–2110, <https://doi.org/10.1021/ef502457p>.
- [49] S.S. Bello, C. Wang, M. Zhang, H. Gao, Z. Han, L. Shi, F. Su, G. Xu, A review on the reaction mechanism of hydrodesulfurization and hydrodenitrogenation in heavy oil upgrading, *Energy Fuel* 35 (14) (2021) 10998–11016, <https://doi.org/10.1021/acs.energyfuels.1c01015>.
- [50] Y. Song, S. Liu, P. Sun, W. Qiu, Y. Li, C. Peng, Catalytic and engineering strategies for enhanced hydrogenation reactions: a review of heterogeneous catalysts and

- process optimization, *RINENG* 25 (2025) 103958, <https://doi.org/10.1016/j.rineng.2025.103958>.
- [51] A.M. Aitani, Oil Refining and Products, Elsevier, N. Y., 2004, <https://doi.org/10.1016/B0-12-176480-X/00259-X>.
- [52] N.T. Nguyen, K.H. Kang, H.H. Pham, K.S. Go, D.V. Pham, P.W. Seo, N.S. Nho, C. W. Lee, S. Park, Catalytic hydrocracking of vacuum residue in a semi-batch reactor: effect of catalyst concentration on asphaltene conversion and product distribution, *J. Ind. Eng. Chem.* 102 (2021) 112–121, <https://doi.org/10.1016/j.jiec.2021.06.033>.
- [53] S. Summers, Y. Zhang, Catalytic hydrotreatment of biocrude from hydrothermal liquefaction of wet-waste: effect of parameters and catalysts on upgraded fuel properties, *Chem. Eng. J. Adv.* 25 (2026) 101008, <https://doi.org/10.1016/j.cej.2025.101008>.
- [54] B.S. Yoon, C. Kim, G.-J. Park, S.G. Jeon, C.H. Ko, Upgrading waste plastic pyrolysis oil via hydrotreating over sulfur-treated Ni-Mo/Al₂O₃ catalysts, *Fuel* 369 (2024) 131688, <https://doi.org/10.1016/j.fuel.2024.131688>.
- [55] G. Escalona, A. Rai, P. Betancourt, A.K. Sinha, Selective poly-aromatics saturation and ring opening during hydroprocessing of light cycle oil over sulfided Ni-Mo/SiO₂-Al₂O₃ catalyst, *Fuel* 219 (2018) 270–278, <https://doi.org/10.1016/j.fuel.2018.01.134>.
- [56] M.P. Squicciarini, Paraffin, olefin, naphthene, and aromatic determination of gasoline and JP-4 jet fuel with supercritical fluid chromatography, *J. Chromatogr. Sci.* 34 (1) (1996) 7–12, <https://doi.org/10.1093/chromsci/34.1.7>.
- [57] F. Pradelle, S.L. Braga, A.R.F.A. Martins, F. Turkovics, R.N.C. Pradelle, Gum formation in gasoline and its blends: a review, *Energy Fuel* 29 (12) (2015) 7753–7770, <https://doi.org/10.1021/acs.energyfuels.5b01894>.
- [58] R.C.C. Pereira, V.M.D. Pasa, Effect of mono-olefins and diolefins on the stability of automotive gasoline, *Fuel* 85 (12) (2006) 1860–1865, <https://doi.org/10.1016/j.fuel.2006.01.022>.
- [59] G. de la Puente, U. Sedran, Formation of gum precursors in FCC naphthas, *Energy Fuel* 18 (2) (2004) 460–464, <https://doi.org/10.1021/ef0340312>.
- [60] S. Mondal, K. Chattopadhyay, B. Srivastav, K. Garg, R. Kumar, A. Chopra, J. Christopher, G.S. Kapur, Dynamic approach for the estimation of olefins in cracked fuel range products of variable nature and composition by 1H NMR spectroscopy, *Energy Fuel* 33 (2) (2019) 1114–1122, <https://doi.org/10.1021/acs.energyfuels.8b04392>.
- [61] Q. Xin, A. Alvarez-Majmutov, H.D. Dettman, J. Chen, Hydrogenation of olefins in bitumen-derived naphtha over a commercial hydrotreating catalyst, *Energy Fuel* 32 (5) (2018) 6167–6175, <https://doi.org/10.1021/acs.energyfuels.8b00344>.
- [62] M. Badawi, L. Vivier, G. Pérot, D. Duprez, Promoting effect of cobalt and nickel on the activity of hydrotreating catalysts in hydrogenation and isomerization of olefins, *J. Mol. Catal. A Chem.* 293 (1) (2008) 53–58, <https://doi.org/10.1016/j.molcata.2008.07.006>.
- [63] S. Ding, S. Jiang, J. Wang, X. Huang, Z. Yang, Effects of the Ni-Mo ratio on olefin selective hydrogenation catalyzed on Ni-Mo-S active sites: a theoretical study by DFT calculation, *Fuel* 277 (2020) 118136, <https://doi.org/10.1016/j.fuel.2020.118136>.
- [64] P. Rahimi, C. Fairbridge, M. Oballa, C. Wong, A. Somogyvari, Effect of hydrotreating on the stability of synthetic crude from western canada, *Prepr. Symp. Am. Chem. Soc., Div. Fuel Chem.* 43 (1) (1998) 13–17.
- [65] D.D. Pham, T.M. Nguyen, T.H. Ho, Q.V. Le, D.L.T. Nguyen, Advancing hydrodesulfurization in heavy Oil: recent developments, challenges, and future prospects, *Fuel* 372 (2024) 132082, <https://doi.org/10.1016/j.fuel.2024.132082>.
- [66] P.R. Robinson, G.E. Dolbear, Hydrotreating and hydrocracking: fundamentals, in: C.S. Hsu, P.R. Robinson (Eds.), *Practical Advances in Petroleum Processing*, Springer New York, New York, NY, 2006, pp. 177–218.
- [67] A. Dimitriadis, L.P. Chrysikou, G. Meletidis, G. Terzis, M. Auersvald, D. Kubicka, S. Bezergianni, Bio-based refinery intermediate production via hydrodeoxygenation of fast pyrolysis bio-oil, *Renew. Energy* 168 (2021) 593–605, <https://doi.org/10.1016/j.renene.2020.12.047>.
- [68] S.S. Bello, C. Wang, M. Zhang, Z. Han, L. Shi, K. Wang, Z. Zhong, F. Su, G. Xu, Recycling the CoMo/Al₂O₃ catalyst for effectively hydro-upgrading shale oil with high sulfur content and viscosity, *RSC Adv.* 10 (61) (2020) 37287–37298, <https://doi.org/10.1039/D0RA07419E>.
- [69] I. Hita, A. Gutiérrez, M. Olazar, J. Bilbao, J.M. Arandes, P. Castaño, Upgrading model compounds and scrap Tires Pyrolysis Oil (STPO) on hydrotreating NiMo catalysts with tailored supports, *Fuel* 145 (2015) 158–169, <https://doi.org/10.1016/j.fuel.2014.12.055>.
- [70] Z. Islam Rony, M. Mofijur, M.M. Hasan, M.G. Rasul, M.I. Jahirul, S. Forruque Ahmed, M.A. Kalam, I. Anjum Badruddin, T.M. Yunus Khan, P.-L. Show, Alternative fuels to reduce greenhouse gas emissions from marine transport and promote UN sustainable development goals, *Fuel* 338 (2023) 127220, <https://doi.org/10.1016/j.fuel.2022.127220>.
- [71] F. Lin, M. Xu, K.K. Ramasamy, Z. Li, J.L. Klinger, J.A. Schaidle, H. Wang, Catalyst deactivation and its mitigation during catalytic conversions of biomass, *ACS Catal.* 12 (21) (2022) 13555–13599, <https://doi.org/10.1021/acscatal.2c02074>.
- [72] G.H.C. Prado, Y. Rao, A. de Klerk, Nitrogen removal from oil: a review, *Energy Fuel* 31 (1) (2017) 14–36, <https://doi.org/10.1021/acs.energyfuels.6b02779>.
- [73] C. Polischuk, J. Elezea, S. Vedachalam, A.K. Dalai, J. Adjaye, A review of foulant sources, operational issues, and remedies during the processing of oil sand derived bitumen fractions, *Fuel* 340 (2023) 127516, <https://doi.org/10.1016/j.fuel.2023.127516>.
- [74] P. Dufresne, Hydroprocessing catalysts regeneration and recycling, *Appl. Catal. A Gen.* 322 (2007) 67–75, <https://doi.org/10.1016/j.apcata.2007.01.013>.
- [75] K. Kohli, R. Prajapati, S.K. Maity, M. Sau, M.O. Garg, Deactivation of hydrotreating catalyst by metals in resin and asphaltene parts of heavy oil and residues, *Fuel* 175 (2016) 264–273, <https://doi.org/10.1016/j.fuel.2016.02.036>.
- [76] C. Song, An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel, *Catal. Today* 86 (1) (2003) 211–263, [https://doi.org/10.1016/S0920-5861\(03\)00412-7](https://doi.org/10.1016/S0920-5861(03)00412-7).
- [77] X.-Q. Yao, Y.-W. Li, H. Jiao, Mechanism of thiophene hydrodesulfurization on a MoS₃S9 model catalyst. A computational study, *J. Mol. Struct. THEOCHEM* 726 (1) (2005) 81–92, <https://doi.org/10.1016/j.theochem.2005.02.074>.
- [78] K. Konuma, H. Hasegawa, K. Itabashi, Electronic effect of the second hetero atom on the hydrodesulfurization of heterocyclic Sulphur compounds, *Appl. Catal. 38* (1) (1988) 109–118, [https://doi.org/10.1016/S0166-9834\(00\)80990-2](https://doi.org/10.1016/S0166-9834(00)80990-2).
- [79] G.-N. Yun, K.-D. Kim, Y.-K. Lee, Hydrotreating of waste tire pyrolysis oil over highly dispersed Ni₂P catalyst supported on SBA-15, *Catalysts* 11 (11) (2021) 1272, <https://doi.org/10.3390/catal11111272>.
- [80] S.A. Ali, S. Ahmed, K.W. Ahmed, M.A. Al-Saleh, Simultaneous hydrodesulfurization of dibenzothiophene and substituted dibenzothiophenes over phosphorus modified CoMo/Al₂O₃ catalysts, *Fuel Process. Technol.* 98 (2012) 39–44, <https://doi.org/10.1016/j.fuproc.2012.01.027>.
- [81] M. Egorova, R. Prins, Hydrodesulfurization of dibenzothiophene and 4,6-dimethylidibenzothiophene over sulfided NiMo/γ-Al₂O₃, CoMo/γ-Al₂O₃, and Mo/γ-Al₂O₃ catalysts, *J. Catal.* 225 (2) (2004) 417–427, <https://doi.org/10.1016/j.jcat.2004.05.002>.