

Potential Application of Plant-Mediated Zirconia by Hydrothermal Method for Microwave-Assisted Bio-Jet Fuel Production

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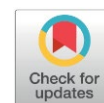
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Received: 21th August 2026; Revised: 24th September 2026; Accepted: 24th September 2026
Available online: 29th September 2026; Published regularly: December 2026



Abstract

Waste and biomass valorization provide promising routes for biofuel production while addressing environmental challenges associated with conventional feedstocks and energy-intensive processing. In this study, plant-mediated zirconia (ZrO₂) was hydrothermally prepared using *Sapindus rarak* extract (SPE) and evaluated as a catalyst for microwave-assisted hydroprocessing of used cooking oil (UCO) and *Calophyllum inophyllum* L. oil (CIO). Phenolic compounds and saponins were the predominant constituents of SPE, while the prepared ZrO₂ exhibited a predominantly tetragonal crystalline structure, nanoscale particles, and mesoporous characteristics attributed to interparticle voids. Under microwave irradiation at 550 °C, with an H₂ flow rate of 20 mL.min⁻¹, a catalyst-to-oil mass ratio of 1:100 (w/w), and a reaction time of 30 min, the prepared ZrO₂ promoted the formation of C₈–C₁₆ hydrocarbons with a higher paraffin fraction compared with commercial monoclinic ZrO₂ and catalyst-free treatment. Bio-jet fuel selectivity and yield reached 56.03% and 19.51 wt% for UCO and 48.90% and 15.72 wt% for CIO, respectively. Three consecutive reuse cycles with UCO resulted in a gradual decline in bio-jet fuel yield, accompanied by changes in product distribution and the retention of organic species on the catalyst. Altogether, these findings indicate the potential of plant-mediated ZrO₂ for microwave-assisted hydroprocessing of waste-derived and non-edible oils, while further catalyst development is needed to improve catalytic performance and product quality.

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Keywords: Biofuel production; hydrothermal preparation; microwave-assisted catalysis; nanomaterial; zirconia

How to Cite: Saviola, A. J., Trisunaryanti, W., Syoufian, A., Salmayanti, U. K., Saputri, W. D., Amin, A. K., Wijaya, K. (2026). Potential Application of Plant-Mediated Zirconia by Hydrothermal Method for Microwave-Assisted Bio-Jet Fuel Production. *Bulletin of Chemical Reaction Engineering & Catalysis*, 21 (4), 989-1006. (DOI: 10.9767/bcrec.20823)

Permalink/DOI: <https://doi.org/10.9767/bcrec.20823>

1. Introduction

In the twenty-first century, growing demand for aviation fuel and the need to reduce dependence on petroleum-derived energy sources have stimulated increasing interest in renewable alternatives for the aviation sector. Aviation is

particularly challenging to decarbonize because of its high energy-density requirements and continued dependence on liquid hydrocarbon fuels, making renewable drop-in alternatives an important component of the transition toward more sustainable aviation [1]. Bio-jet fuel produced from renewable and waste-derived feedstocks has emerged as a promising pathway for aviation fuel production, offering compatibility

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with existing fuel infrastructure and aircraft engines while providing opportunities to reduce life-cycle greenhouse-gas emissions relative to petroleum-derived jet fuel [2]. Among the available conversion pathways, hydroprocessed esters and fatty acids (HEFA) is one of the most technologically mature routes for producing jet fuel-range hydrocarbons (C_8 – C_{16}) from triglycerides and fatty acids and has demonstrated considerable potential for producing hydrocarbon fuels suitable for aviation applications [3].

Renewable and waste-derived oils containing triglycerides and fatty acids represent important feedstocks for HEFA-based bio-jet fuel production. Among these, non-edible oils have attracted increasing global interest over the past decade because of their availability across diverse regions [4]. Used cooking oil (UCO) is particularly attractive because of its widespread availability, low economic value, and potential to address waste-management concerns while providing a source of value-added hydrocarbon fuels [5,6]. Non-edible oils such as *Calophyllum inophyllum* L. oil (CIO) are also of interest because of their substantial fatty acid content, particularly C_{16} and C_{18} species. However, their potential for bio-jet fuel production remains relatively underexplored, despite the ability of these fatty acids to undergo hydroprocessing and generate hydrocarbons within the desired jet fuel range [7]. The use of both waste-derived and non-edible oils can therefore broaden the feedstock basis for bio-jet fuel production. During hydroprocessing, triglycerides and fatty acids undergo a series of catalytic transformations, including hydrodeoxygenation, decarboxylation, decarbonylation, and subsequent hydrocracking, to produce hydrocarbons within the jet fuel fraction [8].

Despite the technological maturity of HEFA, conventional hydroprocessing generally relies on external conductive or convective heating, which can result in inefficient heat transfer, prolonged heating periods, and substantial energy consumption, particularly in heterogeneous catalytic systems. Microwave-assisted hydroprocessing has therefore emerged as an alternative heating strategy because microwave irradiation enables rapid volumetric energy transfer and direct interaction with microwave-responsive components within the reaction system [9]. This approach can facilitate rapid heating, minimize thermal gradients, and shorten processing times, making microwave irradiation attractive for catalytic hydroprocessing [10].

The effectiveness of microwave-assisted hydroprocessing is strongly influenced by the physicochemical characteristics of the catalyst. Suitable surface area, pore architecture, thermal stability, and acid properties can facilitate

deoxygenation and hydrocarbon-chain transformations while providing accessible sites for triglycerides, fatty acids, and their reaction intermediates [11]. Zirconia (ZrO_2) is particularly attractive as an oxide catalyst because of its high thermal and chemical stability, tunable surface acid properties, and strong interactions with active species [12,13]. Its structural robustness is advantageous under the elevated temperatures required for catalytic hydroprocessing. The physicochemical properties of zirconia are also influenced by the conditions used during its preparation, including the chemical environment and processing route. Controlling these parameters is therefore important for obtaining zirconia with properties suitable for catalytic applications.

Conventional preparation of zirconia-based materials frequently employs synthetic structure-directing agents or surfactants, such as cetyltrimethylammonium bromide (CTAB), Pluronic P-123, and sodium dodecyl sulfate (SDS), to regulate nucleation, particle growth, and pore development [14–16]. Although effective, these additives can increase material-processing costs and raise environmental concerns because of their toxicity, persistence, and limited biodegradability. Plant-derived biomolecules have consequently attracted interest as alternatives because they provide naturally occurring organic compounds that can participate in inorganic-material formation. In particular, *Sapindus rarak*, an indigenous Indonesian plant, contains abundant saponins with amphiphilic characteristics that have been utilized as natural mediators in the preparation of nanomaterials for catalytic applications [17,18]. These saponins can interact with precursor species during material formation and may influence the nucleation and growth of zirconia particles. Thus, *Sapindus rarak* extract (SPE) provides a plant-mediated approach based on a locally available Indonesian biological resource.

Hydrothermal treatment offers a suitable route for zirconia preparation because the combined effects of elevated temperature and autogenous pressure can promote crystallization and particle formation under controlled conditions [19,20]. Adding SPE to this process provides an alternative means of controlling zirconia formation using plant-derived constituents. However, the application of SPE-mediated zirconia prepared by a hydrothermal route to microwave-assisted hydroprocessing of triglyceride- and fatty acid-rich feedstocks remains limited. Accordingly, this study investigates hydrothermally prepared zirconia using SPE as a catalyst for microwave-assisted hydroprocessing of UCO and CIO as representative waste-derived and non-edible renewable feedstocks, respectively. The material

was characterized in terms of its structural, textural, and surface properties and evaluated for its catalytic performance in producing jet fuel-range hydrocarbons. This work provides insight into the applicability of SPE-mediated zirconia for microwave-assisted hydroprocessing of different triglyceride- and fatty acid-rich feedstocks.

2. Materials and Methods

2.1 Materials

The chemical reagents employed in this study included zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 99%) and ammonium hydroxide (NH_4OH , 25%), both of analytical grade. *Sapindus rarak* extract (SPE), commercially marketed as *lerak liquid soap*, was obtained from a local supplier in Yogyakarta, Indonesia. Used cooking oil (UCO) was collected from a local food vendor in Yogyakarta, Indonesia, while *Calophyllum inophyllum* L. oil (CIO) was purchased from an online supplier, with the oil originating from Purworejo, Indonesia. Deionized water was obtained from CV Bima Aksara Nusa, Indonesia. Hydrogen gas (99% purity) was supplied by PT Samator Indo Gas Tbk, Indonesia. Commercial monoclinic ZrO_2 (99%) obtained from Jiaozuo Huasu, China, was used as a reference catalyst.

2.2. Phytochemical Analysis of *Sapindus rarak* Extract

2.2.1. Total alkaloid content

The alkaloid content of SPE was quantified using the bromocresol green (BCG) method with quinine as the reference standard. Briefly, 1 mL of SPE was acidified with 5 mL of 2 N HCl and washed three times with 10 mL of chloroform. The aqueous phase was then neutralized with 0.1 N NaOH, followed by the addition of 5 mL each of BCG solution and phosphate buffer. The resulting mixture was extracted three times with 5 mL of chloroform at 500 rpm for 15 min per extraction. The combined chloroform fractions were evaporated under nitrogen, redissolved in chloroform, and adjusted to a final volume of 5 mL. The absorbance was measured at 470 nm, and the alkaloid content was calculated from the quinine calibration curve.

2.2.2. Total saponin content

For saponin quantification, 0.25 mL of SPE was first subjected to acid hydrolysis using 2 mL of 25% H_2SO_4 in an autoclave at 110 °C for 120 min. Following hydrolysis, the sample was extracted with diethyl ether, and the resulting filtrate was evaporated to dryness. The residue was reconstituted in 1 mL of water and vortex-mixed for 5 min. An aliquot of anisaldehyde (50 μL) was then added and allowed to react for 10

min, after which 2 mL of 50% H_2SO_4 was added. The reaction mixture was heated at 60 °C for 10 min, made up to 10 mL, and subjected to fivefold dilution. The absorbance was measured at 435 nm, and the saponin concentration was calculated using the corresponding calibration curve.

2.2.3. Total tannin content

Tannin quantification was performed using the Folin–Ciocalteu colorimetric method, with tannic acid as the calibration standard. Briefly, 0.25 mL of SPE was extracted with 10 mL of diethyl ether for 20 h, followed by filtration and solvent evaporation. The resulting residue was reconstituted with distilled water to a final volume of 10 mL. Subsequently, 1 mL of the solution was combined with 0.1 mL of Folin–Ciocalteu reagent and 2 mL of 20% sodium carbonate solution, and the mixture was further diluted to 10 mL. After standing at room temperature for 30 min, the absorbance was measured at 760 nm. The tannin content was then calculated using the calibration curve established with tannic acid.

2.2.4. Total phenolic content

Phenolic compounds were quantified using the Folin–Ciocalteu assay with gallic acid as the standard. To establish the calibration curve, 10 mg of gallic acid was reacted with 0.5 mL of Folin–Ciocalteu reagent and 7.5 mL of distilled water for 10 min. Subsequently, 1.5 mL of 20% sodium carbonate solution was added, and the resulting mixture was maintained at 40 °C for 20 min. The reaction was immediately quenched by cooling in an ice bath, followed by dilution to a final volume of 10 mL. The absorbance was measured at 760 nm, and the phenolic content was determined from the resulting gallic acid calibration curve.

2.2.5. Total flavonoid content

Flavonoids were quantified using a colorimetric method with quercetin as the reference standard. Briefly, 10 mg of quercetin was reacted with 0.3 mL of 5% NaNO_2 for 5 min, followed by the addition of 0.6 mL of 10% AlCl_3 and a further 5 min reaction period. Subsequently, 2 mL of 1 M NaOH was added, and the solution was diluted to 10 mL with distilled water. The absorbance was measured at 510 nm, and the flavonoid content was calculated from the quercetin calibration curve.

2.3. Preparation and Characterization of Zirconia (ZrO_2)

2.3.1. Preparation of zirconia (ZrO_2)

Zirconia was prepared through a hydrothermal route mediated by SPE, with the

preparation procedure schematically illustrated in Figure 1. Initially, 100 mL of SPE was mixed with 50 mL of deionized water, followed by the addition of 6.45 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ under continuous stirring at 300 rpm. Subsequently, 25% NH_4OH solution was added dropwise while maintaining continuous stirring until the pH reached 10, resulting in gel formation. The gel was then transferred into an autoclave and hydrothermally treated at 100 °C for 4 h. Following hydrothermal treatment, the resulting material was recovered and repeatedly washed with deionized water until chloride ions were no longer detected. The washed material was separated by centrifugation at 3000 rpm for 30 min and subsequently dried at 100 °C for 6 h. The dried solid was then ground and passed through a 270-mesh sieve. Finally, the resulting powder was calcined in a muffle furnace at 500 °C for 3 h to obtain the ZrO_2 catalyst.

2.3.2. Characterization of zirconia (ZrO_2)

The physicochemical properties of the prepared ZrO_2 were investigated using complementary characterization techniques. X-ray diffraction (XRD, Aeris Benchtop) identified the crystalline phases, while Fourier-transform infrared spectroscopy (FTIR, Bruker Alpha II) analyzed the surface functional groups. Surface morphology and elemental composition were examined using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS, JEOL JED-2300) and field-emission scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (FESEM-EDS, JEOL JSM-6510LA). Transmission electron microscopy (TEM, Talos F200X) was used to examine particle morphology

and primary particle size. The hydrodynamic particle-size distribution was determined by dynamic light scattering (DLS, Anton Paar). Textural properties were evaluated by nitrogen adsorption-desorption using a Micromeritics Gemini VII instrument, while total acidity was assessed by temperature-programmed desorption of ammonia (NH_3 -TPD, Micromeritics Chemisorb 2750). Thermal stability was evaluated using a simultaneous thermal analyzer (STA 6000) over the temperature range of 25–1000 °C at a heating rate of 10 °C.min⁻¹.

2.4. Hydroprocessing Experiments

Microwave-assisted catalytic hydroprocessing was performed at 550 °C under a continuous H_2 flow of 20 mL min⁻¹ and atmospheric pressure. A catalyst-to-oil mass ratio of 1:100 (w/w) was employed, corresponding to 10 mg of catalyst and 1000 mg of oil. The reaction was conducted in a semi-batch reactor configuration, in which the catalyst and oil were placed in separate chambers, with the catalyst positioned in the upper section and the oil in the lower section of the reactor tube. The reactor was housed in a modified microwave oven operating at 2.45 GHz and capable of delivering up to 800 W of power. A schematic illustration of the reactor configuration and experimental setup is presented in Figure 2.

Following hydroprocessing for 30 min, the condensable products were collected as the liquid product, while the catalyst was recovered for reuse in the subsequent hydroprocessing cycle. The liquid product was analyzed by gas chromatography-mass spectrometry (GC-MS, Shimadzu QP2010S) equipped with a DB-5MS capillary column (30 m × 0.25 mm × 0.25 µm). The

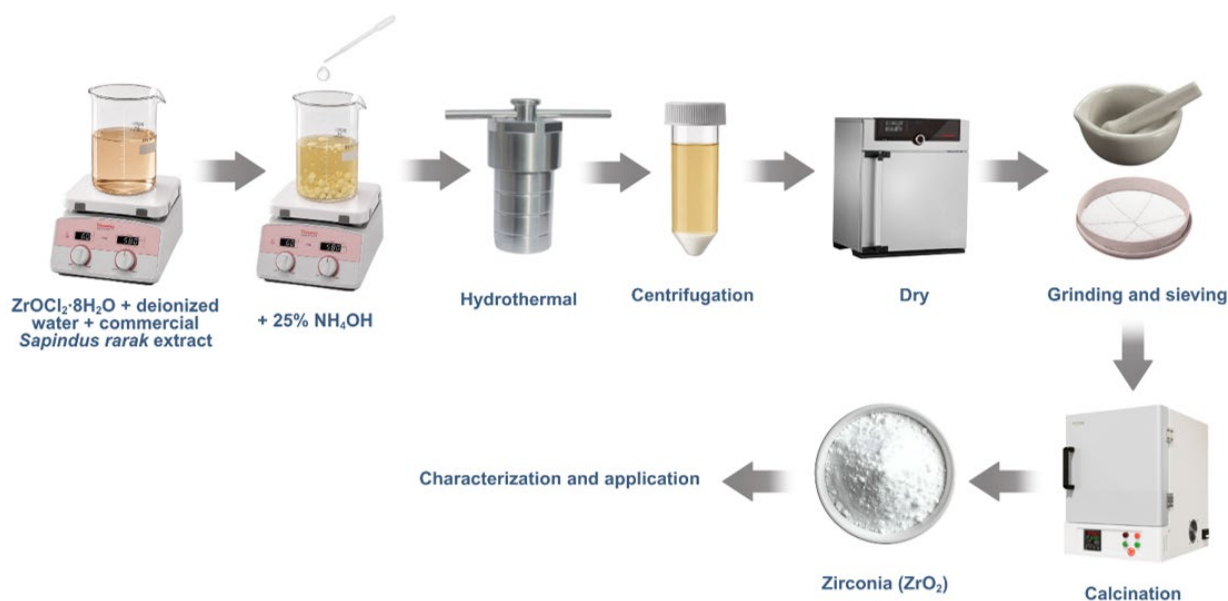


Figure 1. Flowchart illustrating the preparation procedure of ZrO_2 .

product distribution was determined from the mass balance of the liquid product, coke, residual oil, and gaseous products according to Equations (1)–(4). Bio-jet fuel selectivity was determined from the relative GC peak areas of hydrocarbons within the C₈–C₁₆ range, while the corresponding bio-jet fuel yield was calculated from the liquid-product yield and C₈–C₁₆ selectivity using Equations (5) and (6), respectively.

$$\text{Liquid product (wt\%)} = \frac{\text{mass of collected liquid product (g)}}{\text{mass of initial oil (g)}} \times 100 \quad (1)$$

$$\text{Coke (wt\%)} = \frac{\text{mass of spent catalyst (g)} - \text{mass of fresh catalyst (g)}}{\text{mass of initial oil (g)}} \times 100 \quad (2)$$

$$\text{Residual oil (wt\%)} = \frac{\text{mass of residual oil (g)}}{\text{mass of initial oil (g)}} \times 100 \quad (3)$$

$$\text{Gas product (wt\%)} = (100 - \text{liquid product} - \text{gas} - \text{residual oil}) \quad (4)$$

$$\text{Bio-jet fuel selectivity (\%)} = \frac{\text{GC area of C}_8 \text{ to C}_{16}}{\text{total GC area}} \times 100 \quad (5)$$

$$\text{Bio-jet fuel yield (wt\%)} = \frac{\text{GC area of C}_8 \text{ to C}_{16}}{\text{total GC area}} \times \text{liquid product} \quad (6)$$

3. Results and Discussion

3.1. Analysis of *Sapindus rarak* Extract

Figure 3(a) presents the phytochemical composition of the commercial *Sapindus rarak* extract (SPE) used as a plant-derived mediator in the zirconia preparation. Phenolic compounds and saponins were the predominant constituents, whereas tannins, flavonoids, and alkaloids were present at lower levels. Saponins are naturally occurring surface-active compounds with an amphiphilic structure comprising a hydrophobic sapogenin moiety and hydrophilic sugar groups [21,22]. This structural arrangement enables interactions with both aqueous and relatively nonpolar environments, thereby imparting surfactant-like properties that may influence particle nucleation, growth, and dispersion during material formation [23,24]. Phenolic compounds, in contrast, contain oxygen-bearing functional groups, particularly hydroxyl groups, that can interact with metal species through coordination or chelation [25]. Such interactions may facilitate the association of zirconium-containing species with organic constituents during precursor transformation and contribute to the stabilization of developing particles. Accordingly, the coexistence of abundant saponins and phenolic

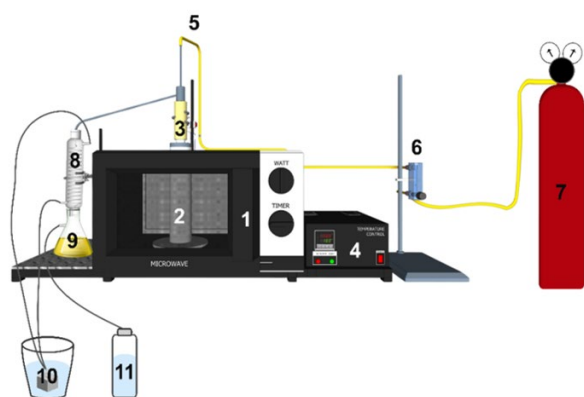


Figure 2. Schematic illustration of the hydroprocessing reactor and experimental setup. (1) Microwave oven, (2) reactor tube containing separate catalyst and oil chambers, (3) reactor seal, (4) temperature controller, (5) hydrogen inlet, (6) flowmeter, (7) hydrogen cylinder, (8) condenser, (9) liquid-product vessel, (10) water pump, and (11) gas outlet.

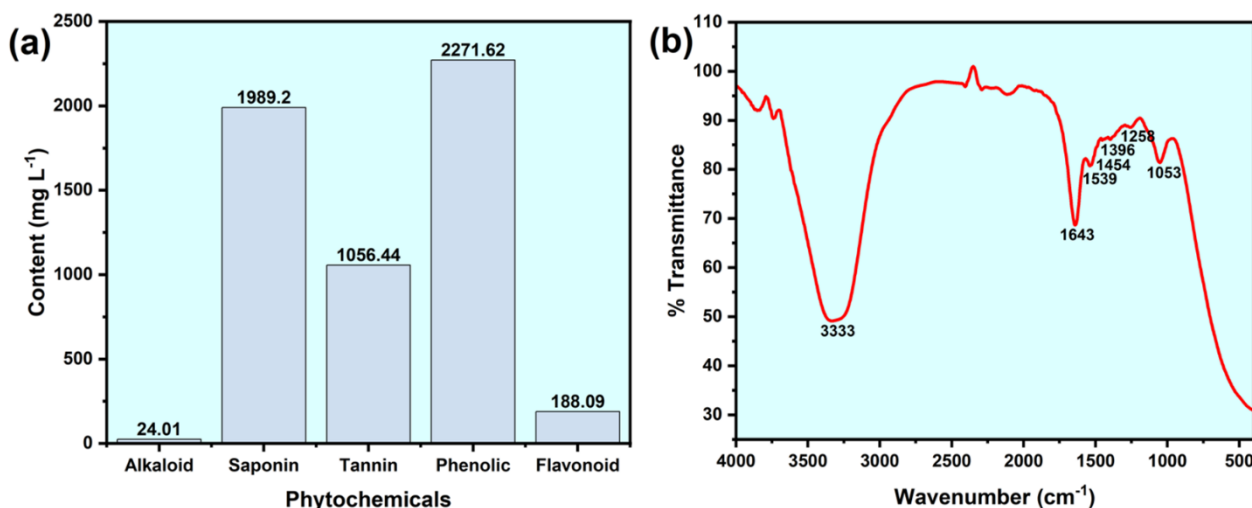


Figure 3. Phytochemical content (a) and FTIR spectrum (b) of SPE.

compounds provides a plausible chemical basis for the role of SPE in the plant-mediated formation of ZrO_2 .

Further information on the organic constituents of SPE is provided by the FTIR spectrum in Figure 3(b). A broad band at 3333 cm^{-1} is mainly attributed to O–H stretching, reflecting hydroxyl-containing constituents and/or hydrogen-bonded water. The band at 1643 cm^{-1} is predominantly associated with H–O–H bending of molecular water, consistent with the aqueous nature of the extract. Additional bands at 1539 , 1454 , 1396 , 1258 , and 1053 cm^{-1} arise from vibrations of carbon- and oxygen-containing functional groups within the organic constituents. In particular, the bands near 1258 and 1053 cm^{-1} can be associated with C–O and C–O–C vibrations, respectively, consistent with glycosidic functionalities commonly present in saponins [26]. The band around 1396 cm^{-1} may also involve vibrations of aliphatic groups associated with triterpenoid or sapogenin structures. Collectively, the phytochemical and FTIR analyses indicate

that SPE contains surface-active and oxygen-containing constituents capable of interacting with zirconium species during material formation.

3.2. Characterization of the Prepared ZrO_2

Crystalline phase identification of the prepared ZrO_2 was first performed by XRD, as shown in Figure 4(a). Well-resolved reflections appeared at 2θ values of approximately 30.02° , 35.15° , 50.24° , 59.98° , 62.67° , 74.38° , and 81.72° , which were indexed to the (101), (110), (112), (211), (202), (220), and (213) planes of tetragonal ZrO_2 , respectively, based on JCPDS No. 01-079-1769 [27]. A weak reflection at approximately 28.07° , assigned to the (–111) plane of monoclinic ZrO_2 , was also observed, indicating the presence of a minor monoclinic phase. The crystallite sizes estimated using the Debye–Scherrer equation [Equation (7)] from the monoclinic (–111) and tetragonal (101) reflections were 16.20 and 32.55 nm , respectively. Using the Garvie–Nicholson

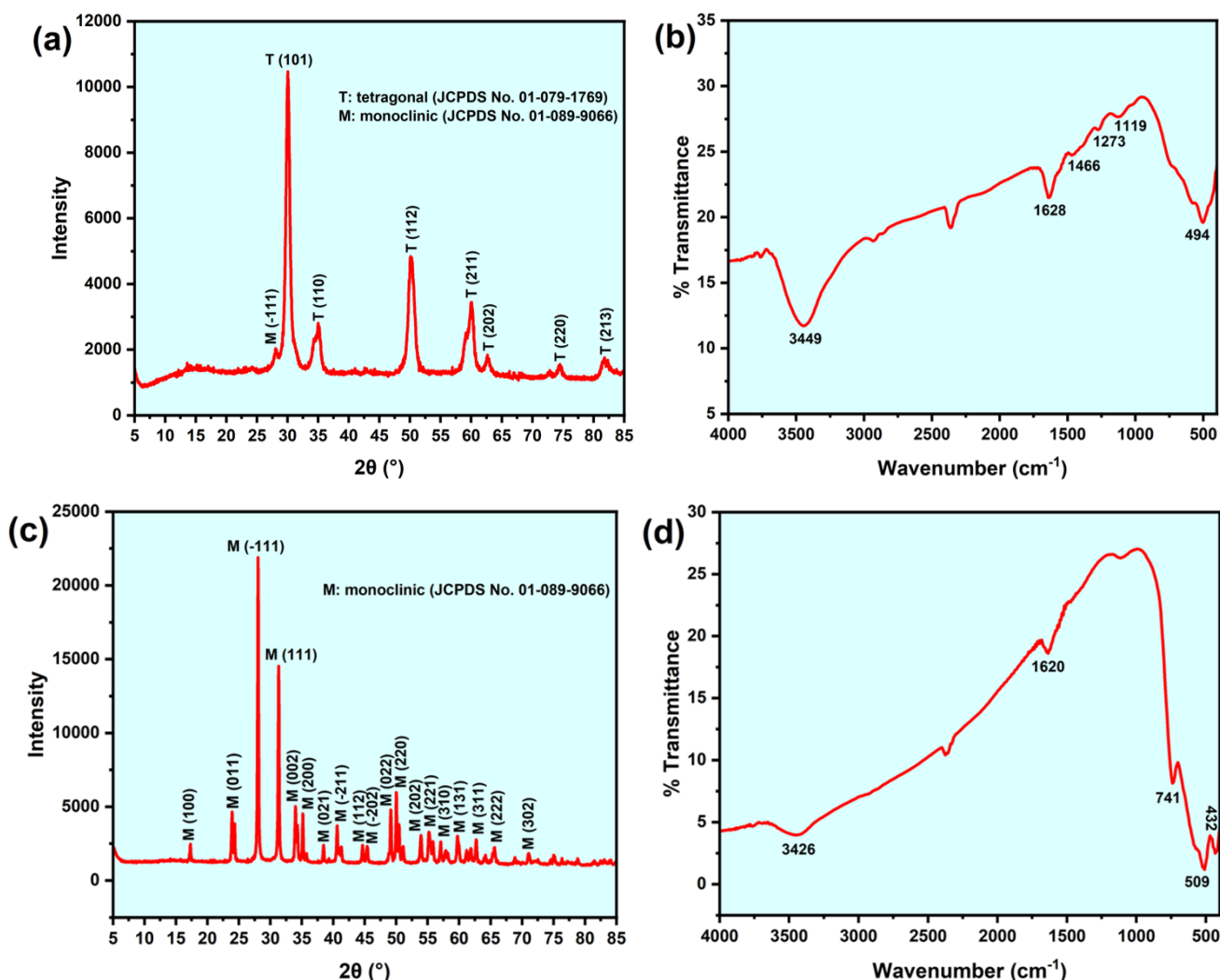


Figure 4. XRD pattern (a) and FTIR spectrum (b) of the prepared ZrO_2 ; XRD pattern (c) and FTIR spectrum (d) of commercial monoclinic ZrO_2 .

equation [Equation (8)], with the intensity of the monoclinic (111) reflection set to zero because no distinct reflection was observed, the monoclinic fraction (X_m) was calculated as 16.25%. The corresponding monoclinic volume fraction (V_m), calculated using the Toraya equation [Equation (9)], was 20.28%, giving a tetragonal volume fraction of 79.72%. Thus, the prepared ZrO_2 was predominantly tetragonal, with a minor monoclinic contribution.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (7)$$

$$X_m = \frac{I_m(-111) + I_m(111)}{I_m(-111) + I_m(111) + I_t(101)} \quad (8)$$

$$V_m = \frac{1.311 \times X_m}{1 + 0.311 \times X_m} \quad (9)$$

Complementary information on the chemical functionalities of the prepared ZrO_2 is provided by the FTIR spectrum in Figure 4(b). A broad absorption band around 3449 cm^{-1} is mainly associated with O–H stretching, whereas the band at 1628 cm^{-1} can be attributed to O–H bending of adsorbed water. Additional bands around 1466, 1273, and 1119 cm^{-1} can be associated with C–O and C–O–C vibrations, suggesting the presence of residual oxygen-containing organic species from

the plant-mediated synthesis. The absorption band around 494 cm^{-1} is attributable to Zr–O-related vibrations, supporting the formation of the zirconium oxide framework [28].

For comparison, the XRD pattern of the commercial ZrO_2 in Figure 4(c) exhibits the characteristic diffraction pattern of monoclinic ZrO_2 , indexed according to JCPDS No. 01-089-9066. The corresponding FTIR spectrum in Figure 4(d) displays bands associated with adsorbed water, including a broad band around 3426 cm^{-1} and a band at 1620 cm^{-1} . The bands at approximately 741, 509, and 432 cm^{-1} are associated with Zr–O vibrations [29].

Morphological and elemental characteristics of the prepared ZrO_2 were subsequently examined by SEM–EDS and TEM. The SEM image in Figure 5(a) reveals an irregular, highly aggregated morphology with relatively rough and heterogeneous surface features. Such aggregation is commonly observed in oxide nanomaterials because the high surface energy of small particles promotes interparticle interactions during drying and calcination. The EDS spectrum in Figure 5(b) shows Zr and O as the principal detected elements, consistent with the expected composition of zirconia. Elemental mapping in Figure 5(c) further shows a relatively uniform distribution of Zr and O throughout the

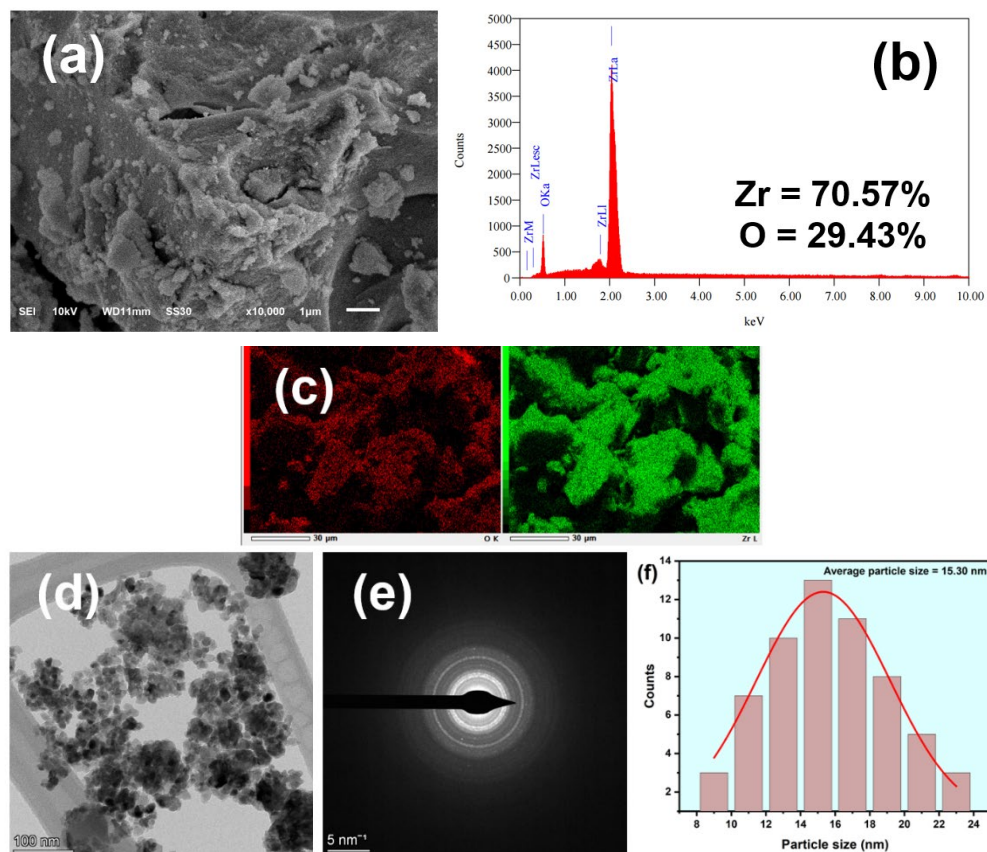


Figure 5. SEM image at a scale bar of $1\text{ }\mu\text{m}$ (a), EDS spectrum (b), elemental mapping images at a scale bar of $30\text{ }\mu\text{m}$ (c), TEM image at a scale bar of 100 nm (d), SAED pattern (e), and particle-size distribution based on measurements of 60 particles (f) of the prepared ZrO_2 .

analyzed region, without apparent macroscopic elemental segregation.

Nanoscale morphology was subsequently examined by TEM, as shown in Figure 5(d). The particles exhibit irregular shapes and form aggregates, consistent with the SEM observations. Measurement of 60 particles yielded an average particle size of 15.30 nm, as presented in Figure 5(f). Several concentric diffraction rings are visible in the SAED pattern in Figure 5(e), demonstrating the polycrystalline nature of the prepared material and supporting the crystalline phases identified by XRD. The TEM-derived particle size is smaller than the crystallite sizes estimated from XRD because the two techniques characterize different physical dimensions. TEM measures the dimensions of individual particles, whereas XRD estimates the size of coherently diffracting crystalline domains from diffraction-peak broadening. Differences in particle morphology, sampling, and the assumptions inherent to the Scherrer equation can therefore produce different size estimates. Collectively, the SEM, TEM, and SAED observations indicate that the prepared ZrO_2 consists of nanosized polycrystalline particles with a pronounced tendency toward aggregation.

Figure 6(a) shows the morphology of the commercial monoclinic ZrO_2 , which also exhibits an irregular and aggregated structure. The EDS spectrum in Figure 6(b) shows Zr and O signals consistent with the expected composition of ZrO_2 , while the elemental mapping in Figure 6(c) indicates a relatively uniform spatial distribution of both elements throughout the analyzed region.

The dispersion characteristics of the prepared ZrO_2 were evaluated by DLS, as shown in Figure

7. An average hydrodynamic diameter of 110.3 ± 3.9 nm and a polydispersity index (PDI) of 0.144 ± 0.007 were obtained from ten measurements. The intensity-based distribution exhibits a single dominant population centred near $0.1 \mu\text{m}$, indicating a relatively narrow distribution of dispersed ZrO_2 entities under the measurement conditions. The substantially larger hydrodynamic diameter than the 15.30 nm particle size determined by TEM is expected because the two techniques characterize different physical dimensions. TEM measures individual solid particles, whereas DLS determines the hydrodynamic diameter of dispersed particles or particle assemblies, which can be affected by aggregation, the surrounding solvation layer, and surface-associated species [30]. Residual or adsorbed constituents originating from SPE may also contribute to the measured hydrodynamic diameter. Accordingly, the DLS value is more

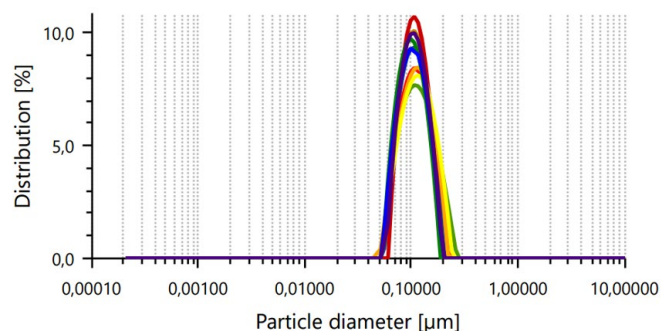


Figure 7. Particle-size distribution of ZrO_2 determined by DLS. The data represent ten measurements.

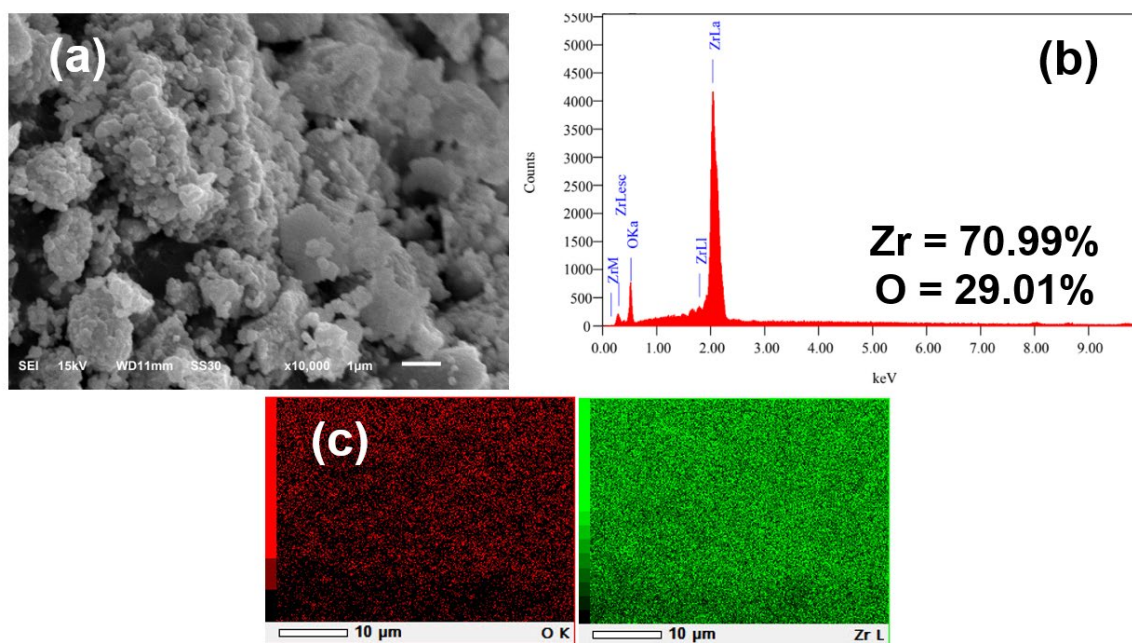


Figure 6. SEM image at a scale bar of $1 \mu\text{m}$ (a), EDS spectrum (b), and elemental mapping images at a scale bar of $10 \mu\text{m}$ of commercial monoclinic ZrO_2 .

appropriately interpreted as the size of dispersed particle assemblies rather than the intrinsic primary particle size. The relatively low PDI indicates a comparatively narrow distribution of the dispersed entities despite the aggregation observed in the dried material [31]. These findings are consistent with the SEM and TEM observations and suggest that nanosized zirconia particles form larger hydrodynamic assemblies in suspension.

The textural properties of the prepared ZrO_2 were investigated by N_2 adsorption–desorption analysis, as shown in Figure 8(a). The isotherm can be classified as a Type IV(a) isotherm with an H2-type hysteresis loop, indicating mesoporous characteristics and suggesting a relatively complex pore network with possible pore-blocking or pore-constriction effects [32]. The prepared ZrO_2 exhibits a specific surface area of $32.58 \text{ m}^2 \cdot \text{g}^{-1}$, calculated using the Brunauer–Emmett–Teller (BET) method, together with a total pore volume of $0.06 \text{ cm}^3 \cdot \text{g}^{-1}$ and an average pore diameter of 4.10 nm . The average pore diameter falls within the mesoporous range, supporting the presence of mesoporosity. The moderate specific surface area may be associated with the crystalline structure and particle aggregation observed by XRD, SEM, and TEM, which can restrict the development of a larger accessible surface area. Nevertheless, the mesoporous structure provides accessible regions for interactions between reactant molecules and the ZrO_2 surface.

The pore-size distribution was evaluated using the Barrett–Joyner–Halenda (BJH)

method, as presented in Figure 8(b). A predominantly mesoporous distribution is observed, with a notable contribution in the $4\text{--}7 \text{ nm}$ range, consistent with the average pore diameter obtained from the adsorption analysis. These pores may originate from the packing of aggregated nanosized ZrO_2 particles and the resulting interparticle voids, together with pores within the material structure [33]. Such textural characteristics indicate that particle aggregation does not completely restrict pore accessibility, allowing the prepared ZrO_2 to retain an accessible porous network.

Total acidity was evaluated by NH_3 -TPD, as shown in Figure 8(c). A broad NH_3 desorption region was observed from 100 to $500 \text{ }^\circ\text{C}$, with a pronounced contribution between 200 and $300 \text{ }^\circ\text{C}$ followed by a gradual decrease at higher temperatures. This profile indicates acid sites with different interaction strengths. The total acidity was $0.20 \text{ mmol} \cdot \text{g}^{-1}$, indicating a measurable population of acidic sites on the prepared ZrO_2 . These sites may be associated with surface zirconium species, including coordinatively unsaturated Zr^{4+} centers, and surface hydroxyl groups [34]. The O–H functionalities identified by FTIR provide complementary evidence for hydroxyl-containing surface environments. Thus, the NH_3 -TPD results demonstrate that the prepared ZrO_2 possesses measurable total acidity arising from its surface chemical characteristics.

In contrast, the N_2 adsorption–desorption isotherm of the commercial monoclinic ZrO_2 in Figure 8(d) exhibits substantially lower N_2

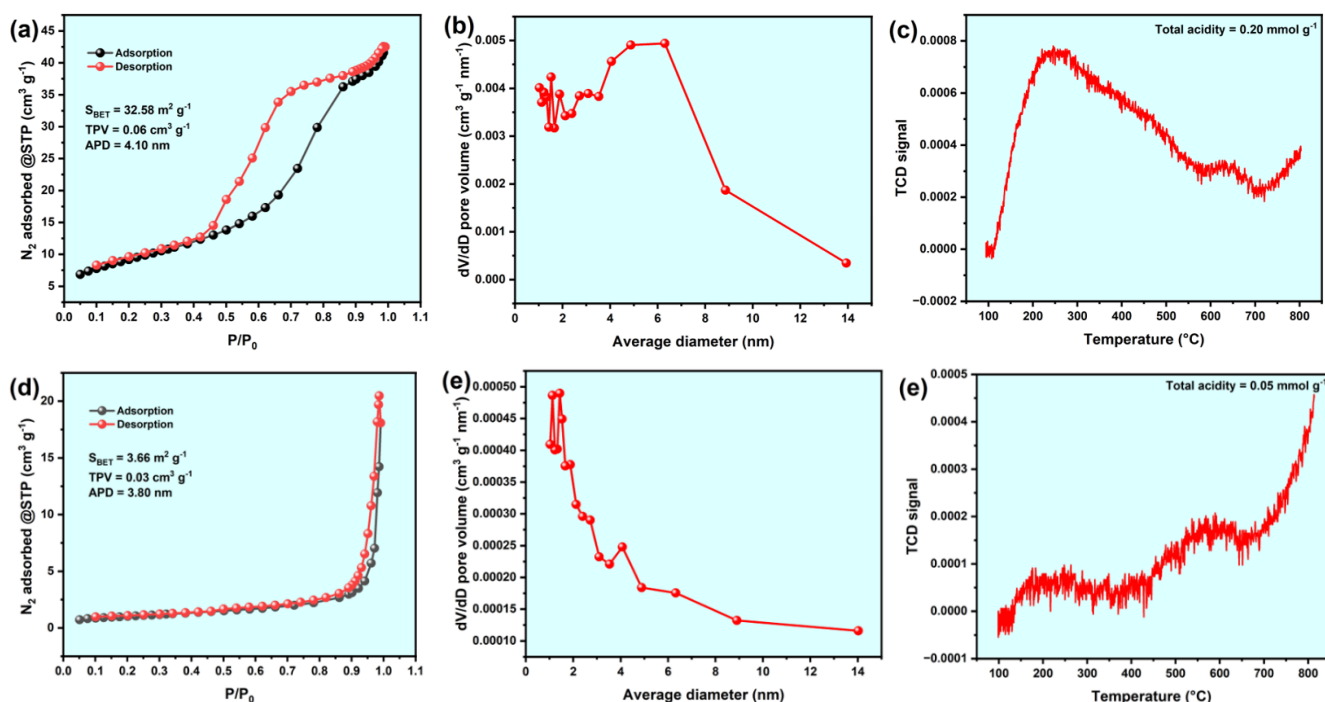


Figure 8. N_2 adsorption–desorption isotherm, pore size distribution, and NH_3 -TPD profile of the prepared ZrO_2 (a–c) and commercial monoclinic ZrO_2 (d–f).

uptake than the prepared ZrO_2 , indicating a lower accessible surface area. The commercial sample has a specific surface area of $3.66 \text{ m}^2\cdot\text{g}^{-1}$, a total pore volume of $0.03 \text{ cm}^3\cdot\text{g}^{-1}$, and an average pore diameter of 3.80 nm. These values indicate limited development of accessible porosity relative to the prepared ZrO_2 . The pore-size distribution in Figure 8(e) also shows a small contribution to the pore volume across the analyzed diameter range, consistent with the low total pore volume.

The acidity of the commercial monoclinic ZrO_2 was also lower, as shown by the NH_3 -TPD profile in Figure 8(f). NH_3 desorption occurred over a broad temperature range, indicating acid sites with different interaction strengths. The total acidity was $0.05 \text{ mmol}\cdot\text{g}^{-1}$, substantially lower than that of the prepared ZrO_2 . Altogether, the prepared ZrO_2 exhibits a larger specific surface area and total pore volume, together with higher total acidity, than the commercial monoclinic reference. These differences may provide greater accessibility to surface sites for reactant interactions and are relevant to the subsequent comparison of their catalytic performance.

3.3. Catalytic Performance Evaluation

The catalytic performance of the hydrothermally prepared ZrO_2 was evaluated using used cooking oil (UCO) and *Calophyllum inophyllum* L. oil (CIO) as feedstocks. Their fatty acid compositions, determined by GC-MS, are summarized in Table 1. Both feedstocks were dominated by oleic acid, while UCO contained a higher proportion of palmitic acid and CIO contained relatively higher proportions of linoleic and stearic acids. Thus, the two feedstocks differed in their fatty acid chain-length distribution and degree of unsaturation. These compositional differences can influence the distribution of products formed during hydroprocessing because the chain length and degree of unsaturation of fatty acid-derived compounds affect their subsequent hydrogenation, deoxygenation, and C-C bond-cleavage reactions.

Product distributions obtained from thermal (catalyst-free) and ZrO_2 -assisted treatments are presented in Figure 9(a). For UCO, ZrO_2 increased the liquid fraction and decreased the gas fraction, while only a small amount of coke was detected. A similar distribution was observed for CIO. At 550°C , thermal cracking can promote C-C bond cleavage of long-chain fatty acid-derived compounds, resulting in lighter hydrocarbons and gaseous products [35]. The higher liquid fraction obtained with ZrO_2 therefore indicates a change in the distribution of products toward condensable compounds under the investigated conditions.

The effect of ZrO_2 on product distribution is further reflected in the carbon-number profiles in Figure 9(b). Catalyst-free treatment of UCO generated hydrocarbons across a relatively broad carbon-number range, including products both within and outside the C_8 – C_{16} range. Following ZrO_2 addition, the distribution became more concentrated within C_8 – C_{16} , accompanied by changes in the relative abundance of heavier C_{17} – C_{20} hydrocarbons. CIO exhibited a comparable shift toward the C_8 – C_{16} range after catalyst addition. Because hydrocarbons within C_8 – C_{16} broadly correspond to the jet fuel range, this redistribution indicates that ZrO_2 influenced the carbon-number distribution of the liquid hydrocarbons under the applied conditions [36,37].

The formation of C_8 – C_{16} hydrocarbons can involve a combination of hydrogenation, deoxygenation, and C-C bond cleavage of triglyceride- and fatty acid-derived intermediates. Under a continuous H_2 atmosphere, unsaturated intermediates can undergo hydrogenation, while deoxygenation can proceed through hydrodeoxygenation, decarboxylation, and decarbonylation, with H_2O , CO_2 , and CO formed as the corresponding oxygen-containing products [38–40]. Subsequent C-C bond cleavage of longer-chain hydrocarbons can also contribute to the formation of lower-carbon-number products. The increase in paraffin content accompanied by a decrease in olefins after ZrO_2 addition is consistent with a higher proportion of saturated hydrocarbons in the resulting liquid products.

Microwave irradiation served as the heating mode for the hydroprocessing reactions. Under the applied conditions, microwave heating provides direct energy transfer to the reaction system and enables rapid heating to the reaction temperature [41]. The resulting high-temperature environment can promote thermal and catalytic transformations of triglyceride- and fatty acid-derived compounds. Thus, the

Table 1. GC-MS analysis results for the fatty acid composition of UCO and CIO.

Fatty acid name and formula	Composition in used cooking oil (%)	Composition in <i>Calophyllum inophyllum</i> L. oil (%)
Lauric acid, $\text{C}_{12}\text{H}_{24}\text{O}_2$	0.47	not detected
Myristic acid, $\text{C}_{14}\text{H}_{28}\text{O}_2$	1.18	not detected
Palmitic acid, $\text{C}_{16}\text{H}_{32}\text{O}_2$	37.75	20.33
Oleic acid, $\text{C}_{18}\text{H}_{34}\text{O}_2$	42.28	44.21
Linoleic acid, $\text{C}_{18}\text{H}_{32}\text{O}_2$	13.63	20.97
Stearic acid, $\text{C}_{18}\text{H}_{36}\text{O}_2$	4.40	13.72
Arachidic acid, $\text{C}_{20}\text{H}_{40}\text{O}_2$	0.29	0.77

differences between catalyst-free and ZrO_2 -assisted treatments reflect changes in the liquid-product distribution under microwave-assisted hydroprocessing conditions.

Further information on the chemical composition of the liquid products is provided by the paraffin, iso-paraffin, olefin, naphthene, and aromatic (PIONA) distributions in Figure 9(c). Paraffinic hydrocarbons were the predominant product group for both feedstocks under catalyst-free and ZrO_2 -assisted conditions. ZrO_2 addition increased the paraffin fraction while decreasing the relative contribution of olefins for both UCO and CIO. This change is consistent with hydrogenation of unsaturated compounds under the H_2 atmosphere. Hydrogenation of $\text{C}=\text{C}$ bonds can occur before or concurrently with deoxygenation during hydroprocessing of vegetable oils, resulting in more saturated hydrocarbon products [42]. The lower olefin content after ZrO_2 addition therefore indicates a higher proportion of saturated hydrocarbons in the liquid products.

In contrast, the relatively low iso-paraffin content suggests that extensive skeletal isomerization was not evident under the investigated conditions. Straight-chain paraffins can be formed through deoxygenation of fatty

acid-derived compounds, whereas substantial formation of branched hydrocarbons generally requires suitable hydrogenation–dehydrogenation functionality and acidic sites for skeletal isomerization. The predominance of paraffins and comparatively low iso-paraffin content therefore indicates that the prepared ZrO_2 mainly produced linear saturated hydrocarbons rather than substantial amounts of branched hydrocarbons. Future catalyst development could introduce transition-metal functionalities, such as Ni or Co, into an appropriately acidic support to provide hydrogenation–dehydrogenation functionality and facilitate subsequent hydroisomerization [43,44]. Noble-metal-based bifunctional systems containing Pt or Pd have likewise been investigated for this purpose [45,46].

Oxygenated compounds provide additional information on the composition of the liquid products. Alcohols and aldehyde/ketone compounds remained minor components, indicating that oxygen-containing compounds were substantially converted during hydroprocessing. Their residual presence, however, shows that oxygenated species remained in the liquid products after reaction. These compounds may represent partially

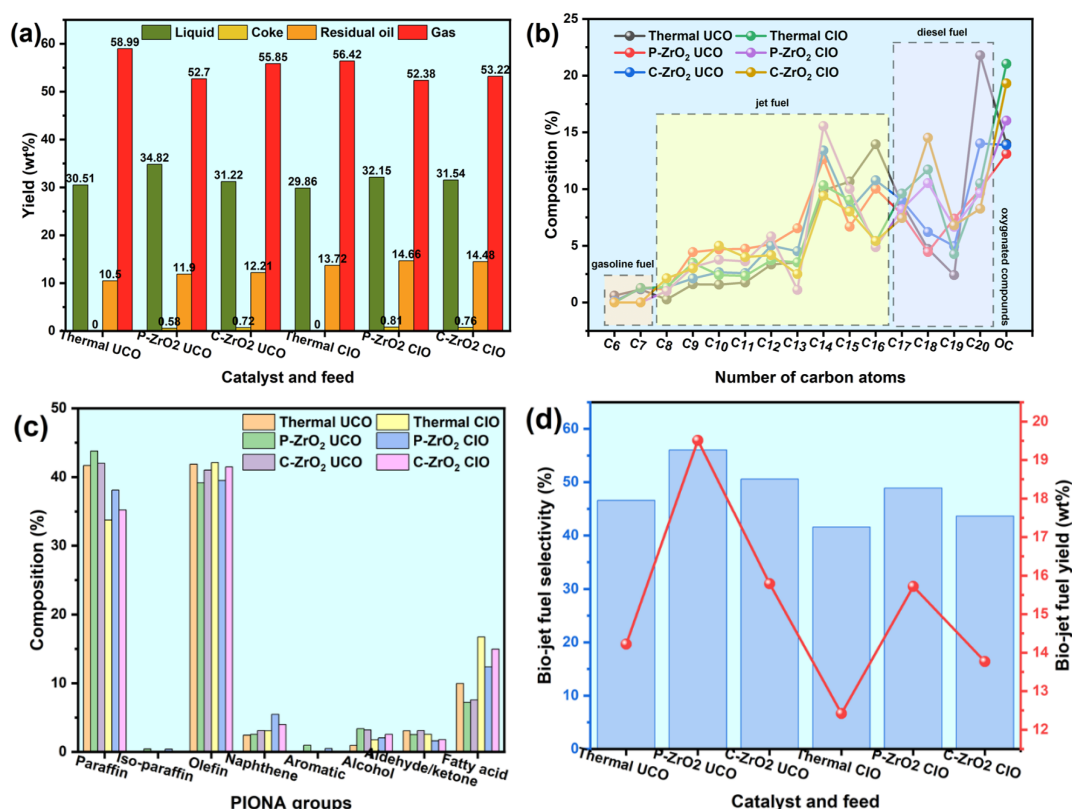


Figure 9. Microwave-assisted catalytic hydroprocessing results of UCO and CIO using the prepared ZrO_2 and commercial monoclinic ZrO_2 : (a) product distribution, (b) carbon-number distribution of liquid hydrocarbons, (c) PIONA-group composition of liquid products, and (d) bio-jet fuel selectivity and bio-jet fuel yield. Reaction conditions: $T = 550\text{ }^\circ\text{C}$, $t = 30\text{ min}$, H_2 flow rate = $20\text{ mL}\cdot\text{min}^{-1}$, atmospheric pressure, catalyst mass = 10 mg, and oil mass = 1000 mg.

converted feedstock-derived intermediates or products formed through incomplete deoxygenation. Thus, the liquid-product composition indicates substantial formation of hydrocarbons while retaining a minor fraction of oxygen-containing compounds.

The changes in carbon-number and PIONA-group distributions are reflected in the bio-jet fuel selectivity and yield shown in Figure 9(d). For UCO, bio-jet fuel selectivity increased from 46.60% under catalyst-free treatment to 56.03% after ZrO_2 addition, while the corresponding selectivity for CIO increased from 41.59% to 48.90%. These increases are consistent with the greater proportion of liquid hydrocarbons within the C_8 – C_{16} range observed after catalyst addition. The corresponding bio-jet fuel yield increased from 14.22 to 19.51 wt% for UCO and from 12.42 to 15.72 wt% for CIO. These increases reflect the combined contribution of the liquid-product fraction and the proportion of C_8 – C_{16} hydrocarbons in the liquid products.

The catalytic performance can be considered in relation to the physicochemical properties of the prepared ZrO_2 . Its mesoporous structure provides accessible pore regions, while its measurable total acidity indicates the presence of acidic surface sites. These characteristics may contribute to interactions between the catalyst surface and feedstock-derived compounds during hydroprocessing. However, the present characterization does not resolve the contributions of individual acid-site types or establish specific reaction pathways. Therefore, the observed catalytic performance is best interpreted in terms of the combined physicochemical characteristics of the prepared ZrO_2 .

A comparison with commercial monoclinic ZrO_2 further highlights these differences. For UCO, commercial ZrO_2 produced a bio-jet fuel selectivity of 50.59% and a yield of 15.79 wt%, compared with 56.03% and 19.51 wt%, respectively, for the prepared material. For CIO, commercial ZrO_2 gave 43.66% selectivity and 13.77 wt% yield, compared with 48.90% and 15.72 wt%, respectively, for the prepared ZrO_2 . The higher bio-jet fuel selectivity and yield obtained with the prepared material coincide with its larger specific surface area (32.58 vs. 3.66 $\text{m}^2\cdot\text{g}^{-1}$) and higher total acidity (0.20 vs. 0.05 $\text{mmol}\cdot\text{g}^{-1}$). These differences may contribute to greater availability of surface sites for interactions with reactant molecules. Nevertheless, the comparison should be interpreted in terms of the collective physicochemical properties of the two materials rather than attributed to a single structural or acidic characteristic.

Differences in the catalytic performance observed for UCO and CIO may also arise from their distinct fatty acid compositions. UCO

contained a higher proportion of palmitic acid, whereas CIO contained greater proportions of linoleic and stearic acids. These differences result in distinct distributions of C_{16} - and C_{18} - derived feedstock components and their degrees of unsaturation, which can affect the composition of the resulting hydrocarbons. Accordingly, the differences in bio-jet fuel selectivity and yield between UCO and CIO may be related to their different fatty acid compositions and the resulting product distributions.

3.4. Reusability of the Prepared ZrO_2

The reusability of the prepared ZrO_2 was evaluated over three consecutive microwave-assisted hydroprocessing cycles using UCO. After each reaction, the catalyst was recovered, weighed, and directly reused without washing, drying, or regeneration. As shown in Figure 10(a), the liquid fraction decreased from 34.82 wt% in the first cycle to 30.12 and 26.58 wt% in the second and third cycles, respectively, accompanied by increased gas formation. The coke fraction also increased gradually, whereas the residual-oil fraction remained relatively similar among the three cycles. These changes indicate a progressive shift in product distribution during direct catalyst reuse.

Thereafter, the carbon-number distributions in Figure 10(b) show that the liquid hydrocarbons remained distributed across a broad carbon-number range, although the relative abundance of individual fractions changed with successive cycles. The corresponding PIONA compositions in Figure 10(c) show a gradual decrease in the paraffin fraction accompanied by an increase in olefins. A modest increase in oxygen-containing compounds, particularly alcohols and aldehyde/ketone groups, was also observed. These changes indicate a shift in the composition of the liquid products during repeated catalyst use, with a lower proportion of saturated hydrocarbons and a greater contribution from residual oxygen-containing compounds.

Bio-jet fuel selectivity decreased from 56.03% in the first cycle to 48.42% and 43.41% in the second and third cycles, respectively, while the corresponding bio-jet fuel yield declined from 19.51 to 14.58 and 11.54 wt% [Figure 10(d)]. The decrease in yield coincided with lower liquid-product recovery and increased gas and coke formation. Because the catalyst was directly reused without regeneration, the gradual accumulation of carbonaceous or other retained species may have reduced the accessibility of surface regions [47]. The increasing coke fraction is consistent with progressive catalyst fouling during repeated use, although the present results do not establish a specific deactivation mechanism.

Further characterization of the recovered ZrO_2 was conducted to examine changes in its physicochemical properties after three consecutive hydroprocessing cycles. The TG profiles in Figure 11(a) show a clear difference between the fresh and spent materials. The fresh ZrO_2 exhibited a small mass loss of approximately 1.21%, followed by relatively stable mass at higher temperatures, whereas the spent catalyst showed a considerably greater mass loss of approximately 12.07% over the investigated temperature range. The additional mass loss is consistent with the presence of adsorbed or deposited organic and carbonaceous species following hydroprocessing. The relatively stable profile at higher temperatures indicates that the inorganic ZrO_2 framework remained thermally stable after repeated reaction.

Changes in the crystalline structure were evaluated by XRD, as shown in Figure 11(b). The characteristic reflections of tetragonal ZrO_2

remained clearly observable after reuse, including the (101), (110), (112), (211), (202), (220), and (213) planes, while the weak monoclinic (-111) reflection was also retained. The crystallite size associated with the monoclinic (-111) reflection decreased from 16.20 nm for the fresh ZrO_2 to 13.50 nm after reuse, whereas the calculated crystallite size of the tetragonal (101) reflection increased from 32.55 to 81.36 nm. The Garvie–Nicholson analysis gave monoclinic fractions (X_m) of 16.25% and 18.15% for the fresh and spent catalysts, respectively, corresponding to monoclinic volume fractions (V_m) of 20.28% and 22.53%, respectively. Accordingly, the tetragonal volume fraction decreased from 79.72% to 77.47%. These results suggest a limited increase in the monoclinic contribution during repeated hydroprocessing, although the spent catalyst remained predominantly tetragonal. The increase in the calculated tetragonal crystallite size represents a

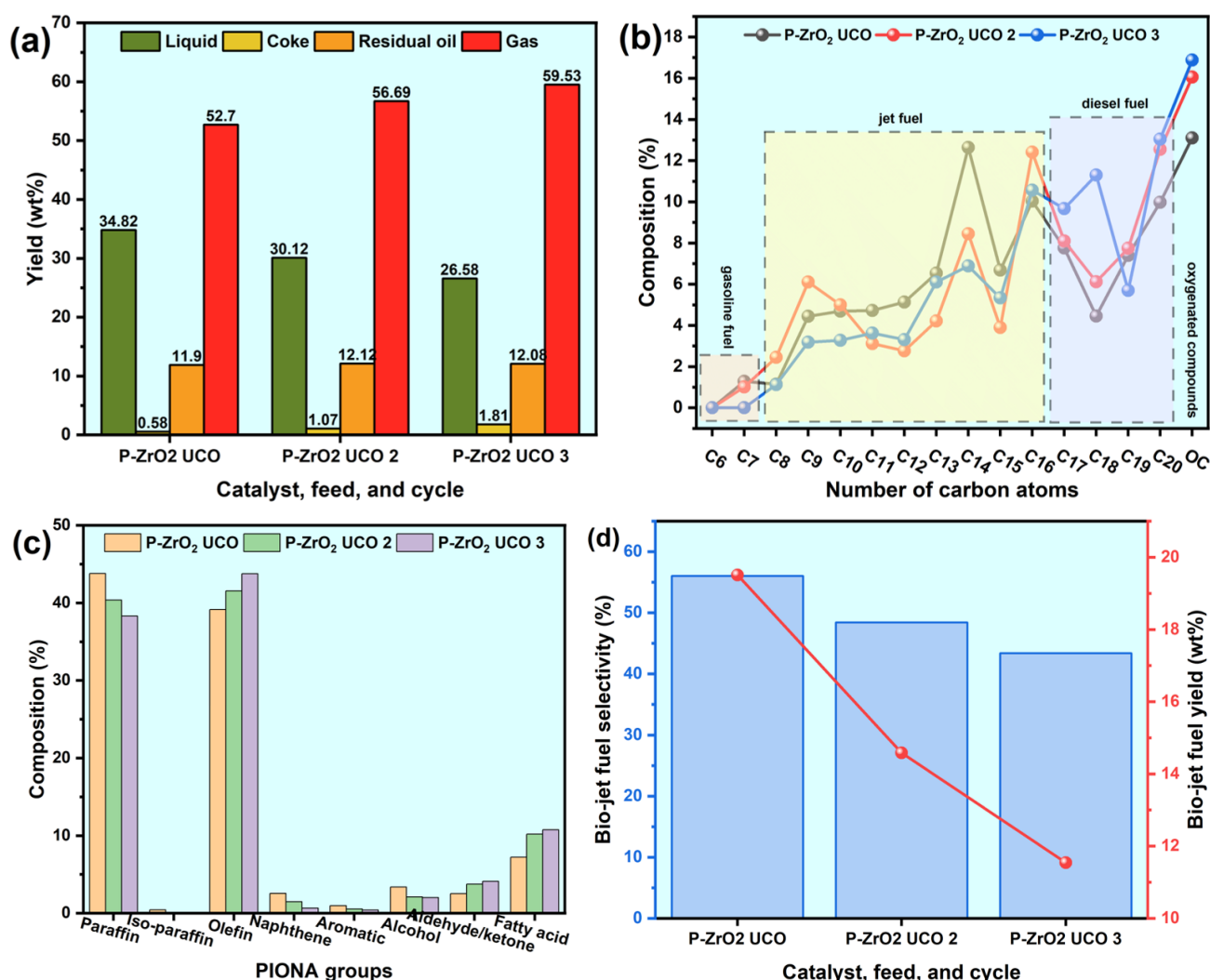


Figure 10. Reusability of the prepared ZrO_2 during three consecutive cycles in microwave-assisted catalytic hydroprocessing of UCO: (a) product distribution, (b) carbon-number distribution of liquid hydrocarbons, (c) PIONA-group composition of liquid products, and (d) bio-jet fuel selectivity and bio-jet fuel yield. Reaction conditions: $T = 550^\circ\text{C}$, $t = 30$ min, H_2 flow rate = $20\text{ mL}\cdot\text{min}^{-1}$, atmospheric pressure, catalyst mass = 10 mg, and oil mass = 1000 mg.

change in the coherently diffracting domain and should not be interpreted directly as particle growth.

After reuse, the FTIR spectrum in Figure 11(c) showed additional bands associated with retained surface species. The fresh ZrO_2 exhibited characteristic bands at approximately 3449 and 1628 cm^{-1} , associated with O–H stretching and bending, respectively, together with Zr–O-related vibrations in the low-wavenumber region. Additional bands appeared at approximately 2924 and 2855 cm^{-1} after reuse, attributable to C–H stretching vibrations, along with a band around 1744 cm^{-1} that can be associated with C=O stretching of carbonyl-containing species [48]. These bands indicate the retention of hydrocarbon-derived and oxygen-containing species on the catalyst surface after repeated hydroprocessing.

The FESEM image and EDS analysis in Figures 11(d–f) provide further evidence of carbon-containing deposits on the recovered catalyst. The spent ZrO_2 retained an aggregated morphology, while the EDS spectrum showed C, O, and Zr as the principal detected elements. Elemental mapping further showed that these elements were distributed throughout the

analyzed region, with carbon broadly detected across the catalyst surface. The substantial carbon contribution is consistent with the presence of carbon-rich deposits. Because EDS provides localized and semiquantitative elemental information, these results should be regarded as evidence of carbon-containing surface deposition rather than as representative of the bulk composition of the spent catalyst.

Altogether, the characterization results indicate that repeated hydroprocessing was accompanied by changes in both the surface composition and crystalline phase distribution of ZrO_2 . The XRD results show a modest increase in the monoclinic contribution while retaining a predominantly tetragonal structure, whereas the TG, FTIR, and EDS results collectively indicate the retention of organic and carbonaceous species. These deposits may restrict access to some surface regions and pores and thereby contribute to the decline in bio-jet fuel selectivity and yield during reuse. Further characterization using nitrogen physisorption, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) would provide additional information on the textural properties, surface composition, and crystalline structure of the

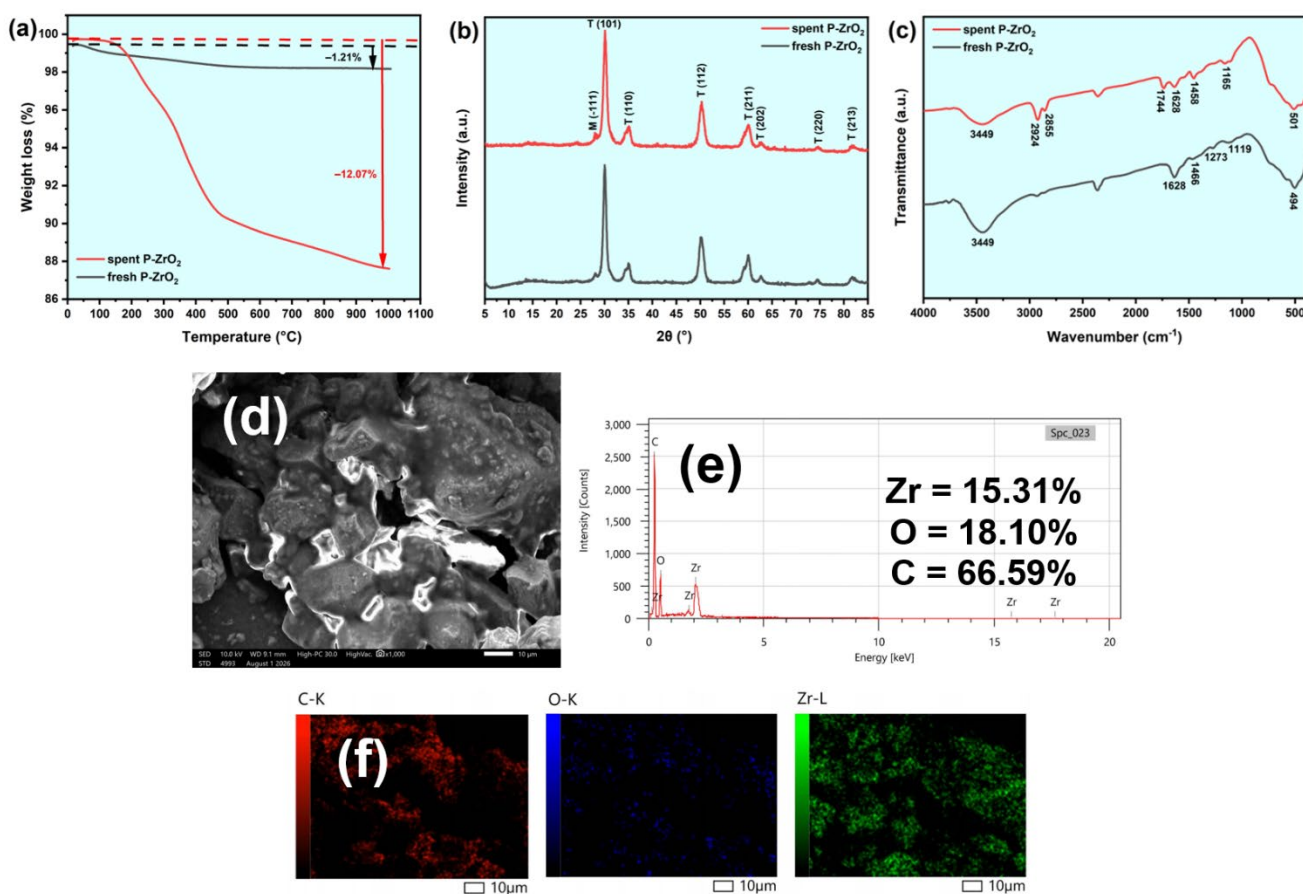


Figure 11. TG profiles (a), XRD patterns (b), and FTIR spectra (c) of fresh and spent ZrO_2 after the reusability test; FESEM image at a scale bar of 10 μm (d), EDS spectrum (e), and elemental mapping images at a scale bar of 10 μm (f) of the spent ZrO_2 .

spent catalyst. Extended cycling and regeneration studies are also needed to determine whether removal of the retained species can restore the catalytic performance of ZrO_2 .

4. Conclusion

In conclusion, ZrO_2 nanomaterial was successfully prepared by hydrothermal treatment using SPE as a plant-derived mediating agent, with phenolic compounds and saponins identified as the predominant phytochemical constituents. The prepared ZrO_2 exhibited an average particle size of 15.30 nm, a DLS hydrodynamic diameter of 110.3 nm, a BET surface area of $32.58 \text{ m}^2\cdot\text{g}^{-1}$, a total pore volume of $0.06 \text{ cm}^3\cdot\text{g}^{-1}$, an average pore diameter of 4.10 nm, and a total acidity of $0.20 \text{ mmol}\cdot\text{g}^{-1}$. The prepared ZrO_2 demonstrated catalytic activity in microwave-assisted hydroprocessing of UCO and CIO, producing bio-jet fuel yields of 19.51 and 15.72 wt%, respectively, under the investigated conditions. After three consecutive cycles using UCO, the bio-jet fuel yield decreased to 11.54 wt%, accompanied by increased coke formation and changes in the liquid-product composition. Further catalyst development, such as acid functionalization or transition-metal introduction, may be explored to improve hydrocarbon formation within the desired jet fuel range.

Acknowledgment

The first author thanks the Center for Environmental Studies, Universitas Gadjah Mada, contract number 1118/UN1/PSLH/PT.01.10/2026 for supporting this research through the *Hibah Publikasi Mahasiswa Pascasarjana*, as well as the Physical Chemistry Laboratory and BRIN Indonesia for providing research facilities for the completion of this doctoral study.

CRedit Author Statement

Author Contributions: A.J. Saviola: Conceptualization, Data Curation, Funding Acquisition, Investigation, Methodology, Visualization, Writing – Original Draft. W. Trisunaryanti: Formal Analysis, Resources, Supervision, Validation. A. Syoufian: Formal Analysis, Supervision, Validation, Writing – Review and Editing. U.K. Salmayanti: Data Curation, Investigation. W.D. Saputri: Data Curation, Resources. A.K. Amin: Supervision, Validation. K. Wijaya: Conceptualization, Project Administration, Supervision, Validation, Writing – Review and Editing. All authors have read and agreed to the published version of the manuscript.

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