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Research Article

The Production of Green Diesel Rich Pentadecane (C15) from Catalytic Hydrodeoxygenation of Waste Cooking Oil using Ni/Al₂O₃-ZrO₂ and Ni/SiO₂-ZrO₂

Momodou Salieu Sowe^{1,2,3}, Arda Rista Lestari¹, Eka Novitasari¹, M. Masruri^{1,2}, Siti Mariyah Ulfa^{1,2,*}

¹Chemistry Department, Faculty of Science, Brawijaya University, Malang, 65145, Indonesia. ²Synthesis and Catalysis of Natural Product Research Group, Faculty of Science, Brawijaya University, Jl.

Veteran, Malang, 65145, Indonesia. ³Chemistry Unit, Division of Physical & Natural Sciences, School of Arts & Sciences, University of The Gambia, The Gambia.

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Abstract

Hydrodeoxygenation (HDO) is applied in fuel processing technology to convert bio-oils to green diesel with metalbased catalysts. The major challenges to this process are feedstock, catalyst preparation, and the production of oxygen-free diesel fuel. In this study, we aimed to synthesize Ni catalysts supported on silica-zirconia and aluminazirconia binary oxides and evaluated their catalytic activity for waste cooking oil (WCO) hydrodeoxygenation to green diesel. Ni/Al₂O₃-ZrO₂ and Ni/SiO₂-ZrO₂ were synthesized by wet-impregnation and hydrodeoxygenation of WCO was done using a modified batch reactor. The catalysts were characterized using X-ray diffraction (XRD), Xray fluorescence (XRF), and scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDS), and N₂ isotherm adsorption-desorption analysis. Gas chromatography - mass spectrometry (GC-MS) analysis showed the formation of hydrocarbon framework n-C₁₅ generated from the use of Ni/Al₂O₃-ZrO₂ with the selectivity of 68.97% after a 2 h reaction. Prolonged reaction into 4 h, decreased the selectivity to 58.69%. Ni/SiO₂-ZrO₂ catalyst at 2 h showed selectivity of 55.39% to n-C₁₅. Conversely, it was observed that the reaction for 4 h increased selectivity to 65.13%. Overall, Ni/Al₂O₃-ZrO₂ and Ni/SiO₂-ZrO₂ catalysts produced oxygen-free green diesel range (n-C₁₄-C₁₈) enriched with n-C₁₅ hydrocarbon. Reaction time influenced the selectivity to n-C₁₅ hydrocarbon. Both catalysts showed promising hydrodeoxygenation activity via the hydrodecarboxylation pathway.

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Keywords:

hydrodeoxygenation; waste cooking oil; green diesel; alumina; zirconia; silica; Ni/Al₂O₃-ZrO₂; Ni/SiO₂-ZrO₂

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1. Introduction

The massive production of CO_2 from the combustion of fossil fuel is suspected to initiate the

* Corresponding Author. Email: ulfa.ms@ub.ac.id (S.M. Ulfa); Telp: +62-341-575835, Fax: +62-341-554403 rapid change in global climate conditions [1]. Consequently, to slow down, the environmental destruction caused by fossil fuel, decreasing dependence on the use of crude oil is one of the choices. Biofuels can be directly obtained from biomass to serve as an alternative, clean and sustainable energy resource to fossil fuel and

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cut down on carbon emissions in the atmosphere. The utilization of biomass [2] and fatty oil [3] renewable feedstock for biofuel production has been reported. Both feedstocks have a problem on a limitation for the mass production of bio-oil, but the low cost and abundant material become an interesting point that may decrease consumption of fossil oil.

Large scale production and the commercial use of the first generation fatty acid methyl ester (FAME) biodiesel is constrained due to high oxygen content which reduces energy density, high viscosity, and poor storage properties [4,5]. Therefore, many researchers are developing different routes for converting fatty oil into biodiesel which is fully compatible with fossil diesel fuel. The second-generation biodiesel is called 'green diesel' that is paraffin-rich diesel that is free from oxygen, sulfur, nitrogen, or aromatic hydrocarbon. The green diesel is produced from the catalytic hydrotreating of renewable feedstock containing triglycerides and fatty acids [6]. Green diesel has a high cetane value and flash value suitable as an alternative fuel for internal combustion engines (ICEs) [7]. Biodiesel production from waste material may ease waste management challenges of waste disposal. Waste cooking oil is an environmentally benign and non-edible feedstock rich in free fatty acid content. Waste cooking oil is a prospective feedstock in catalytic hydrodeoxygenation (HDO) for green diesel production [8].

A series of HDO reactions using WCO feedstock is reported in many aspects. A variety of product distribution mostly heavier straightchain hydrocarbon within the diesel range $(C_{15}-C_{18})$ has previously been generated from waste cooking oil and fatty acids via catalytic hydrodeoxygenation [9]. In a report by [10], the effect of catalyst support on HDO of waste cooking oil was investigated in a stainless steel autoclave reactor. Product distribution is reported to vary between n-C₁₇ and n-C₁₈ hydrocarbon depending on support type. In other reports, n-C₁₇ and n-C₁₈ were detected as major constituents in products obtained from HDO of waste cooking oil [11–13]. The product distribution of hydrocarbon between C₁₅-C₁₈ from biobased feedstock possesses diesel fuel properties similar to conventional diesel with high energy density and good oxidative stability [14].

Heterogeneous bimetallic sulfur-free catalysts, such as NiCu [15], NiMo [16], and NiW [17] on mesoporous and oxide supports, have been studied extensively in the hydrodeoxygenation of fatty acids of vegetable oil to biodiesel. Advantages of heterogeneous Ni-based catalysts are larger active surfaces for better catalytic activity, easy recovery from the reaction mixture, and reusability. Noble metal catalysts have shown outstanding activity in HDO of bio-oil for biodiesel production [12,18]. Despite the high catalytic activity, noble metals are expensive and inflate catalyst production costs. In our previous works, we reported an interesting phase phenomenon with SiO₂ in Ni/ZrO₂-SiO₂ nanocomposite synthesized by the wet impregnation method [19]. SiO₂ underwent crystallinity transformation from crystalline to amorphous due to composite formation with ZrO_2 . A reverse-phase formation from amorphous to crystalline SiO₂ was detected after Ni impregnation. To understand the effect of binary support on Ni catalyst, we tested Ni/SiO₂-ZrO₂ for phenol hydrodeoxygenation in a stainless autoclave batch reactor [20]. The catalyst showed remarkable activity for ring hydrogenation with the selective formation of cyclohexanol and cyclohexanone. In another report, Ni supported by single oxides SiO₂, ZrO₂, and Al₂O₃ were synthesized and tested for phenol hydrodeoxygenation [21]. Ni/SiO₂ showed activity for phenol ring-opening with product formation of 2-methyl-1-butanol and Ni/ZrO₂ promoted hydrogenation leading to the formation of cyclohexanone.

In this work, we synthesized Ni catalysts supported on binary oxides of SiO₂-ZrO₂ and Al_2O_3 - ZrO_2 by the wet impregnation method. Catalyst physicochemical properties, such as: crystalline structure, Ni loading, surface morphology, BET surface area, pore volume, and pore diameter, were studied by XRD, XRF, SEM-EDS, and N₂ isotherm adsorptiondesorption analysis respectively. Catalyst performance was tested for waste cooking oil hydrodeoxygenation to green diesel in a modified batch reactor at 350 °C, 2 MPa H₂, 2 h, and 4 h. All reactions were conducted in a solvent-free environment. Analysis using GC-MS gave the formation of n-C₁₅ as major constituents in green diesel fraction. To our knowledge, this is the first report on the production of green diesel rich with n-C₁₅. It is suggested that the predominant reaction might be catalytic decarboxvlation of the oleic acid.

2. Materials and Methods

2.1 Materials

Analytical grade $ZrOCl_2.8H_2O$ (Merck KGaA) and Ni(NO₃)_{2.6H₂O} (Merck KGaA) were used as precursors for ZrO_2 and Ni-based metal sources. γ -Al₂O₃ (Merck KGaA) and SiO₂ (0.063-0.200 mm) Merck KGaA were used as support materials. Ammonium solution

(NH₄OH), silver nitrate solution (AgNO₃), deionized water (DI), and anhydrous sodium sulfate (Na₂SO₄) were used as received.

2.2 Methods

2.2.1 Catalyst preparation

The binary oxide Al₂O₃-ZrO₂ and SiO₂-ZrO₂ was previously prepared in a 1:1 (wt/wt) ratio according to the reported methods [19,20]. 10 g of Al₂O₃-ZrO₂ was prepared by dissolving 13 g of ZrOCl₂.8H₂O in deionized water (DI) with the dropwise addition of NH₄OH until pH 8 was identified by the formation of $Zr(OH)_4$ as a white precipitate. The precipitate was directly mixed with 5 g of γ -Al₂O₃ which was then aged for 10 h at a constant temperature of 75 °C. After aging, the solid mixture was dried to constant weight and calcined under N₂ gas for 5 h at 500 °C to obtain the Al₂O₃-ZrO₂ composite. The SiO₂-ZrO₂ composite was also prepared by a similar procedure by mixing $10 \text{ g of } SiO_2$ with the Zr(OH)₄ precipitate, aged, dried, and calcinated to give SiO₂-ZrO₂ composite.

The Ni/Al₂O₃-ZrO₂ and Ni/SiO₂-ZrO₂ were prepared by the wet impregnation method, by mixing 7.4 g of Ni(NO₃)₂.6H₂O with 10 g of Al₂O₃-ZrO₂ in DI water. The mixture was agitated overnight and then evaporated to dryness to form a solid mixture. The solid mixture was calcined at 500 °C for 5 h under continuous N₂ gas flow followed by reduction under continuous H₂ gas flow at 500 °C for 5 h to form 15% Ni/Al₂O₃-ZrO₂ (Ni/AZ) and 15% Ni/SiO₂-ZrO₂ (Ni/SZ), respectively.



Figure 1. XRD spectra of (a) Ni/Al_2O_3 -ZrO₂ and (b) Ni/SiO_2 -ZrO₂.

2.2.2 Catalyst characterization

The crystal structures of the catalysts were analyzed using an X-Ray Diffractometer (XRD) PAN Analytical E'xpert Pro operated at 40 kV, 35 mA with Cu-K_a radiation of $\lambda = 1.54060$ and $2\theta = 10^{\circ}-80^{\circ}$. SEM measurements at a scan rate of 1°/min were conducted to determine the catalyst surface morphology. The SEM data were collected from PHENOM. Specific surface area is determined from BET isotherms using nitrogen gas at 77 K measured by Belsorp Mini II (Microtrac BEL) at 77 K. X-Rav Fluorescence (XRF) Pan Analytical Type Minipal 4 was used to determine actual Ni loading on Ni/Al₂O₃-ZrO₂ and Ni/SiO₂-ZrO₂, respectively. Potassium Bromide (KBr) pellets with 400-4000 cm⁻¹ spectral range in a Shimadzu 8400S were used to record the Fourier-Transform Infrared Spectra (FT-IR) of the catalysts.

2.2.3 Waste cooking oil pre-treatment method

Waste cooking oil pre-treatment was conducted according to a report by Li et al. [22]. A 500 g of the waste cooking oil collected from a halal food court center in Brawijaya University was mixed with 700 mL of saturated salt solution and heated at 80 °C for 3 h under continuous magnetic stirring. After heating, the solution was placed in a separatory funnel for 12 h and the upper oil layer was collected and mixed with 500 mL of DI water containing 4 g of activated carbon (AC). The mixture was heated at 80 °C for 3 h with stirring. Afterward, the activated carbon was removed by vacuum filtration and the oil was placed in a separatory funnel for layering. The upper oil layer was collected and dried with anhydrous Na₂SO₄. The Na₂SO₄ was removed by filtration and the obtained oil was then stored in an oven at 105 °C for 12 h.

A 10 g of the pre-treated waste cooking oil was trans-esterified with methanol and NaOH catalyst as reported [23]. The free fatty acid (FFA) content of the oil was determined by Gas Chromatography-Mass Spectrometer injected on a Shimadzu (GCMS QP2010s) with an HP-5MS column and FID detector.

2.2.4 Waste cooking oil hydrodeoxygenation reaction

The hydrodeoxygenation reaction (HDO) was according to published methods by our group [24]. Before the reaction, each catalyst Ni/Al₂O₃-ZrO₂ and Ni/SiO₂-ZrO₂ (0.2 g) was activated by heating at 350 °C for 1 h under 2 MPa H₂ gas in the reactor before each run. HDO reaction was started by inserting 25 mL

of the pre-treated waste cooking oil in the reactor containing the activated catalyst. Each reaction was tested at 350 °C, 2 MPa pure H₂ gas pressure for 2 h and 4 h for each run. The HDO liquid organic products obtained were analyzed using GC-MS injected on a Shimadzu QP2010s. GC-MS analysis was conducted at an oven temperature of 40 °C, gradually increased to 250 °C, and held for 2 mins with a splitless injection mode. The gas pressure was 49.5 kPa at a flow rate of 30 mL/min. A Shimadzu (8400S) Fourier-Transformed Infrared Spectrophotometer instrument was used to analyze the liquid organic products before GC-MS analysis.

3. Results and Discussion

3.1 Catalyst Characterizations

Figure 1 illustrates the XRD patterns of Ni/Al₂O₃-ZrO₂ and Ni/SiO₂-ZrO₂ catalysts. From the patterns, the metallic nickel phase is detected at $2\theta = 44^{\circ}$ (111) and 76° (220) according to JCPDS data 96-210-2279. The absence of NiO at $2\theta = 37^{\circ}$, 43°, and 64° was confirmed [25]. The additional heating at 500 °C for 5 h under H₂ flow completely reduced ionic nickel into metallic nickel. Analysis of the support showed that zirconia is detected in two phases, monoclinic (*m*-ZrO₂) at $2\theta = 30^{\circ}$ and 50°, and tetragonal (*t*-ZrO₂) at $2\theta = 35^{\circ}$, 51°, and 60°, similar to Ulfa *et al.* [19]. Distinctive missing patterns are observed for Al_2O_3 and SiO_2 . This is attributed to the formation of amorphous oxides of Al_2O_3 -ZrO₂ and SiO_2 -ZrO₂ as suggested by Xie *et al.* [26] and Zitouni *et al.* [27].

Table 1 shows the physical properties of Ni/Al₂O₃-ZrO and Ni/SiO₂-ZrO₂ catalysts. X-ray fluorescence (XRF) analysis revealed 15.7 wt% Ni loading on Al₂O₃-ZrO support for Ni/Al₂O₃-ZrO and 16.45 wt% Ni loading on SiO₂-ZrO₂ support for Ni/SiO₂-ZrO₂. The slight wt% Ni increment which differs from the theoretical calculations is attributed to Al₂O₃-ZrO₂ and SiO₂-ZrO₂ support weight loss due to calcination at 500 °C for 5 h before Ni impregnation similarly in a report by Fertal *et al.* [28]. The crystallite size of nickel was determined from the XRD data using Scherrer's equation (Table 1).

In Table 1, the BET surface area and porous structure of SiO₂-ZrO₂ support, Ni/Al₂O₃-ZrO₂, and Ni/SiO₂-ZrO₂ catalysts are exhibited. The specific surface area of SiO₂-ZrO₂ support significantly decreased from 77.591 (m²/g) before Ni impregnation to 17.985 (m²/g), therefore, indicating that Ni addition has resulted in changes in the physical properties of SiO₂-ZrO₂. However, the pore volume and pore diameter of SiO₂-ZrO₂ remained almost the same before and after Ni addition. Compared with Ni/Al₂O₃-ZrO₂ (65.938 m²/g), the S_{BET} results



Figure 2. (a) N_2 isotherm adsorption-desorption showed the hysteresis loop type IV typical of mesoporous catalyst, (b) pore distribution of Ni/SiO₂-ZrO₂ and Ni/Al₂O₃-ZrO₂ are similar.

Table 1. Physical properties of $Ni/Al_2O_3\mathchar`-ZrO_2$ and $Ni/SiO_2\mathchar`-ZrO_2$ showed the increment value of metal loading.

Catalyst	$S_{ m BET}~(m m^2/ m g)^{ m a}$	Pore volume (cm ³ /g) ^b	Pore diameter (nm) ^c	Ni loading (%) ^d	Ni crystallite size (nm) ^e
SiO_2 - ZrO_2	77.591	0.3663	6.819	-	
Ni/Al ₂ O ₃ -ZrO ₂	65.938	0.1537	9.326	15.70	34.54
Ni/SiO_2 - ZrO_2	17.985	0.3045	6.772	16.46	59.60

a.b.c N2 isotherm adsorption-desorption results, ^dXRF results, ^ecalculated from XRD data using Scherrer's equation.

revealed a smaller specific surface area for Ni/SiO₂-ZrO₂ In addition, Ni/SiO₂-ZrO₂ showed a larger pore volume while the pore diameter remained smaller.



Figure 3. FTIR spectra of $Ni/Al_2O_3\text{-}ZrO_2$ (blue) and $Ni/SiO_2\text{-}ZrO_2$ (red).

Isotherm adsorption-desorption of the catalysts is depicted in Figure 2. Ni/Al₂O₃-ZrO₂ and Ni/SiO₂-ZrO₂ showed a hysteresis loop on P/P_o = 0.6–0.8, typical of type IV mesopore catalyst. The hysteresis type H2 suggested that there is a blocking on desorption process suggesting the complex pore system with bottle-ink like pore shape with wide neck size [29]. The pore distribution of Ni/Al₂O₃-ZrO₂ is slightly larger compared to Ni/SiO₂-ZrO₂. This is consistent with a previous study by Ulfa *et al.* [30].

From FT-IR analysis (Figure 3), a strong stretching vibration at 1628 cm⁻¹ indicates the presence of SiO₂ in Ni/SiO₂-ZrO₂ and a weak peak at 974 cm⁻¹ confirms the existence of Si–O–Zr bond. A similar observation is made for Ni/Al₂O₃-ZrO₂ with a peak at 1094 cm⁻¹ for Al–O–Al and a peak at 521 cm⁻¹ showing the presence of Al–O–Zr framework in the catalyst as reported by Zhang *et al.* [31]. The SEM images illustrated in Figure 4 show the morphology of Ni/Al₂O₃-ZrO₂ and Ni/SiO₂-ZrO₂, as a close structure parked with tiny particles of irregular shapes which are attributed to Ni deposition on the surface of the support [30]. A





Element	Wt%	At%
OK	26.32	56.98
AlK	12.70	16.31
ZrL	44.10	16.75
NiK	16.88	09.96
Matrix	Correction	ZAF

Element	Wt%	At%
ОК	30.24	57.34
SiK	19.59	21.16
ZrL	24.01	07.99
NiK	26.15	13.51
Matrix	Correction	ZAF



Figure 4. SEM-EDS analysis of (a) Ni/Al_2O_3 -ZrO₂ and (b) Ni/SiO_2 -ZrO₂ showing surface morphology, elemental content, and distribution.

Table 2. Free fatty acid content from hydrolysis of waste cooking oil.

Free Fatty Acid	Carbon Chain ^{c:x}	% Composition (wt%) ¹
Tetradecanoic acid	$C_{14:0}$	1.28
Hexadecanoic acid	$C_{16:0}$	20.60
9-Octadecenoic acid	$C_{18:1}$	1.70
11-Octadecenoic acid	$C_{18:1}$	75.63
Ethyl octadec-9-enoic acid	$C_{20:1}$	0.79
c:xNumber of carbon and a double bond. ¹ Based	l on GC-MS analysis	

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Figure 5. TIC was obtained from GC-MS analysis of waste cooking oil before each reaction. The main component detected is 11-Octadecenoic acid.



Figure 6. TIC was obtained from GC-MS analysis of products from Ni/Al₂O₃-ZrO₂ (Ni/AZ) and Ni/SiO₂-ZrO₂ (Ni/SZ) at respective reaction times. The main product observed is the n-C₁₅ hydrocarbon framework.

close comparison of the images showed that the surface morphology of Ni/Al₂O₃-ZrO₂ consists of tinier particles than Ni/SiO₂-ZrO₂. The SEM-EDS analysis revealed 16.88 wt% nickel content on the surface of Ni/Al₂O₃-ZrO₂ (Figure 4a) and 26.15 wt% on Ni/SiO₂-ZrO₂ (Figure 4b). The differences in metal distribution on the surface might be explained by different penetration modes of Ni on the SiO₂-ZrO₂ surface which is neglected even in higher metal loading [32].

3.2 Hydrodeoxygenation of Waste Cooking Oil

Before hydrodeoxygenation, WCO was hydrolyzed into free fatty acid using NaOH. The composition of free fatty acid content is tabulated in Table 2. The analysis revealed that 11-Octadecenoic acid is the main fatty acid content in our WCO samples (Figure 5). Our analysis agreed with Toba *et al.* [33], in which the main fatty acid content in a household collected WCO was Octadecenoic acid. Similarly, the Octadecenoic acid was reported as a major fatty acid content in WCO from an unidentified source by Zhang *et al.* [13].

Ni/Al₂O₃-ZrO₂ (Ni/AZ) and Ni/SiO₂-ZrO₂ (Ni/SZ) catalysts were tested for waste cooking oil (WCO) hydrodeoxygenation to green-diesel. The reaction is carried out independently for each variation of the reaction. The product conversion and distribution were determined by GC-MS analysis (Figure 6) using an internal standard.

All reaction conditions are summarized in Table 3. In all reactions, the HDO products conversion is 100% except for the reaction using Ni/AZ at 2 h (entry 1). In this reaction by prolonging the time until 4 h increased the conversion up to 100% (entry 2). For the reaction using Ni/SZ catalyst, either at 2 h or 4 h gave 100% conversion (entry 3, entry 4). It is shown that the HDO reaction using Ni/SZ is faster compared to Ni/AZ. Our results are in line with Lycourghiotis *et al.* [34] and Ding *et al.* [10], on higher conversion rates of waste cooking oil fatty acid with sulfur-free Ni-based catalysts. HDO activity and selectivity can be significantly influenced by catalyst support material. The acidity of support material is an important property to consider. Generally, Al_2O_3 exhibits higher acidic strength than SiO₂ therefore prone to coke formation [35]. In a report by Wu *et al.* [36], the effect of Al_2O_3 and SiO₂ support on Ni₂P catalytic HDO of guaiacol was compared. Al_2O_3 showed higher activity for demethylation (DME) and SiO₂ promoted deoxygenation (DDO). SiO₂ also showed weaker acidic strength with the least coke formation. From our results, it is shown that Ni/SZ facilitated higher deoxygenation leading to better WCO conversion and Ni/AZ promoted demethylation by producing more *n*-C₁₅.

Next, the total green diesel yield is varied from 90.57%-97.12% (Table 3) with a major product yield of n-C₁₅ followed by n-C₁₇. The trend of the product is similar for the use of Ni/AZ and Ni/SZ. It is revealed that both catalysts probably promoted hydrogenation followed by decarboxylation and subsequent carbon-chain cracking to give a series of hydrocarbon products consisting of n-C₁₄ to n-C₁₇ as indicated by Zhang et al. [13]. Ni content on AZ and SZ supports (see XRF analysis in Table 1) contributed to higher yields of $n-C_{15}$ for Ni/AZ and Ni/SZ as observed because of high Ni content enhances carbon-chain cracking due to Ni active species high electron density favorable for C-C bond cleavage [35]. However, product n-C₁₈ gives the lowest distribution among all reactions considering that the complex reaction is preferable during the one-step reaction.

In Figure 7, the effect of reaction time on the product distribution is displayed. Ni/AZ gave a higher yield of n-C₁₅ at 2 h, compared to Ni/SZ under the same reaction time. In this case, the difference in catalyst support and Ni loading and/or distribution should affect the yield of n-C₁₅. In reports by Hellinger *et al.* [37] and Popov *et al.* [38], Al₂O₃ is suggested to show a higher specific surface area than SiO₂. In our case, the higher BET specific surface area of Ni/AZ is suspected to influence the catalytic activity of Ni/AZ due to the adequate space for active Ni⁺ species deposition on the

Table 3. Waste cooking oil HDO product distribution for Ni/Al₂O₃-ZrO₂ (Ni/AZ) and Ni/SiO₂-ZrO₂ (Ni/SZ).

Catalyst	Entry Tim (h)	Time	e Conc. (%) -	Product distribution (%)				Total diesel fraction	Non-diesel hydrocarbon		
		(n)		C_{14}	C_{15}	C_{16}	C17	C18	(%)	C_{13}	C_{12}
Ni/AZ	1	2	95.14	6.96	68.97	5.05	9.59		90.57	4.57	
	2	4	100	7.00	58.69	5.38	20.43	4.02	95.52	3.41	1.06
Ni/SZ	3	2	100	5.41	55.39	6.24	26.17	3.91	97.12	2.89	
	4	4	100	7.65	65.13	4.08	17.97		94.83	5.17	

surface of the AZ support (Table 1, S_{BET} data). It is also observed from the SEM image analysis that Ni/AZ catalyst exhibits a smaller particle size compared to Ni/SZ (Figure 4a, 4b). On the other hand, the SEM-EDS data suggest that the Ni distribution on the surface of Ni/SZ is higher compared to Ni/AZ even though the

total Ni loading is almost similar in both catalysts according to the XRF analysis (Table 1, Ni loading). The high distribution of Ni content observed on the surface of SZ in Ni/SZ (Figure 4b) could be attributed to the better fatty acid conversion for Ni/SZ as suggested by Sánchez-Cárdenas *et al.* [39].





Interestingly, a reserve phenomenon is noticed when the HDO reaction time is prolonged to 4 h. It showed decreasing amount of n-C₁₅ yield for Ni/AZ and an increase of n-C₁₅ by using Ni/SZ. It is predicted that Ni/AZ deactivated in longer reaction time due to a high reaction temperature of 350 °C which agrees with Monnier *et al.* [40], on Al₂O₃ support deactivation under similar experimental conditions used in this study. In Figure 8, the predicted reaction pathway is highlighted.

4. Conclusions

In this study, deposition of Ni into Al₂O₃-ZrO₂ and SiO₂-ZrO₂ composites by wet impregnation gave mesopore catalysts Ni/Al₂O₃-ZrO₂ and Ni/SiO₂-ZrO₂ based on BET adsorptiondesorption analysis. The obtained Ni/Al₂O₃-ZrO₂ and Ni/SiO₂-ZrO₂ were tested for waste cooking oil hydrodeoxygenation to green diesel. Analysis of gas chromatography - mass spectrometry revealed that both catalysts gave green diesel fraction n-C₁₄ to n-C₁₇ with rich content of *n*-C₁₅ fraction. Notwithstanding, Ni/SiO₂-ZrO₂ showed better activity for waste cooking oil conversion even after prolonging the reaction from 2 h to 4 h. While Ni/Al₂O₃-ZrO₂ promoted higher selectivity of *n*-C₁₅ hydrocarbon. Therefore, we conclude that Ni/Al₂O₃-ZrO₂ and Ni/SiO₂-ZrO₂ should be potential catalysts for waste cooking oil conversion to green diesel.

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