

Zinc Aluminate Nano-Catalyst for Green Fuel Production from Used Cooking Vegetable Oil

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Abstract: The pursuit of sustainable and renewable energy has driven research into green fuel production from vegetable oils. Hydrocracking, a promising conversion technique, requires efficient catalysts to enhance reaction kinetics and control product selectivity. This work investigates zinc aluminate nano-catalysts for green fuel synthesis from vegetable oils. Zinc aluminate nano-catalysts were synthesized and analyzed using XRD, SEM, TEM, FTIR, and N₂ physisorption. The ZnAl₂O₄ nanoparticles showed a high surface area of 113m²/g with uniform sub-50 nm particles. The hydrocracking reaction conditions consisted of temperatures from 350 to 450°C, hydrogen pressures of 30, 50, and 70 bar, and liquid hourly space velocities in the range of 1 to 2 h⁻¹. The hydrocracking of used cooking oil was evaluated under different conditions using zinc aluminate nano-catalysts. At 400°C, 1.5 wt.% catalyst loading, 50 bar H₂ pressure at 2 ml/min flow rate, biodiesel yield reached 45%. At 450°C, 1.5 wt.% loading, and 50 bar H₂ at 1 ml/min, biokerosene yield reached 47%. Compared to ZSM-5 zeolites, zinc aluminate demonstrated superior catalytic activity, Zinc aluminate nano-catalysts present a promising pathway for green fuel generation from vegetable oils. Their high activity, selectivity, and stability make them well-suited for efficient and sustainable hydrocracking. This work offers valuable perspectives on zinc aluminate nano-catalyst design and application, advancing environmentally benign and economically viable approaches for green fuel production.

Keywords: Green fuel, Nano catalyst, Hydro-cracking, Biofuel, Waste used cooking oil.

1. Introduction

The increasing concerns about environmental sustainability and the need for renewable energy sources have driven significant interest in the production of green fuels. Vegetable oils, derived from various plant sources, have garnered attention as a potential feedstock for green fuel production due to their renewable nature and abundant availability. Hydrocracking, a catalytic process that involves the reducing complicated hydrocarbon molecules to simpler fragments, more valuable ones, presents a promising approach for converting vegetable oils into lighter hydrocarbon products with improved fuel properties [1]-[3].

Vegetable oils, such as soybean, palm, and rapeseed oils, have gained attention as potential feedstocks for green fuel production due to their renewable nature, wide availability, and chemical composition. These oils are predominantly composed

of triglycerides, which consist of chains of fatty acids linked to a glycerol the supporting structure [3], [4]. However, the high molecular weight and complex structure of triglycerides limit their direct use as transportation fuels. Hydrocracking, a catalytic process that involves the breaking down of triglycerides into smaller hydrocarbon molecules, offers a viable solution to convert vegetable oils into lighter and more valuable fuel components [5].

The hydro-treatment procedure includes hydrocracking. Common hydrotreatment processes that occur during the hydrocracking process include decarboxylation (DCO₂), decarbonylation (DCO), and hydrodeoxygenation (HDO). The decarbonylation process is further classified into two types based on the presence of a catalyst: catalytic processes and thermal reactions [6]. As the temperature escalations, side effects have been documented. The engineering is mainly attentive on anticipation since these adverse effects will diminish yield value. Methanation and reverse water gas shift are two typical side effects. The initial side reaction (water gas shift in reverse) happens when the temperature escalations throughout the decarboxylation course, conveyed by methanation until a particular temperature is achieved. The sole probable side reaction during the decarbonylation procedure is methanation [7]. To achieve efficient and selective hydrocracking of vegetable oils, catalysts play a crucial role. Catalysts promote the desired reactions, enhance reaction rates, and control product selectivity [8]. Among the various catalysts explored, zinc aluminate has emerged as a promising candidate for vegetable oil hydrocracking due to its unique properties and catalytic performance [9].

Catalysts play a crucial role in hydrocracking processes by facilitating the desired reactions and controlling product distribution. Zinc aluminate catalysts have emerged as a promising option for vegetable oil hydrocracking due to their unique properties and catalytic performance [8], [9].

Zinc aluminate (ZnAl₂O₄) is a spinel-type oxide material with a well-defined crystal structure. It exhibits excellent thermal stability and possesses acidic sites, which are essential for promoting hydrocracking reactions [10]. The acidity of zinc aluminate catalysts aids in the activation of carbon-carbon bonds, facilitating the cleavage of these bonds and leading to

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the formation of lighter hydrocarbon products. Additionally, the high surface area of zinc aluminate catalysts provides ample active sites for the adsorption and reaction of reactant molecules, contributing to enhanced catalytic activity [10], [11].

The successful utilization of zinc aluminate catalysts in vegetable oil hydrocracking requires a deep understanding of their structure, synthesis methods, and catalytic performance. Previous studies have demonstrated the effectiveness of zinc aluminate catalysts in various catalytic processes, such as the conversion of biomass, syngas, and petroleum feedstocks. For instance, investigated the use of zinc aluminate catalysts for the catalytic conversion of lignocellulosic biomass into valuable chemicals and reported excellent catalytic activity and stability [12]. Likewise, others have explored the hydrocracking of *n*-hexane over zinc aluminate catalysts and demonstrated its high performance in terms of conversion and selectivity [13]. The acidic nature of zinc aluminate catalysts is particularly advantageous for vegetable oil hydrocracking [13], [14]. The acidity helps in the activation of carbon-carbon bonds in triglycerides, promoting cracking reactions and leading to the formation of lighter hydrocarbon products. The control of acidity in zinc aluminate catalysts can be achieved through various factors, such as the zinc-to-aluminum ratio, calcination temperature, and addition of promoters or modifiers [15]. Fine-tuning the acidity allows for better control over the selectivity of the hydrocracking process, enabling the production of desired fuel components, such as gasoline, diesel, and jet fuel [16].

The purpose of this research is to compare the effect of hydro catalytic cracking operation employing nanosized synthesized particles zinc aluminate and Zeolite (ZNS-5) catalyst on converting used cooking oil into green fuel, as well as to evaluate the product characteristics.

2. Experimental

A. Material and Methods

1) Preparation of Used Cooking Oil

Used Cooking oil from nearby fast-food restaurants in Cairo was gathered. The stage of oil preparation begins with two phases of filtering: First, strain the liquid over a coarse screen to remove any solids. The filtration procedure is then carried out using filter paper to guarantee that solid contaminants are removed. The used cooking oil is then stored in a jar at room temperature. Prior to examination and treatment, the oil is heated and agitated at 110 degrees Celsius for two hours to eliminate any moisture.

2) Preparation of $ZnAl_2O_4$ Nano-Catalyst

Zinc aluminate nanostructures were synthesized in an aqueous medium of zinc nitrate using a co-precipitation method with NH_4OH solution [17]. Typical reaction techniques involved dissolving $Zn(NO_3)_2 \cdot 6H_2O$ (25 mmol) in 15 mL of distilled water and mixing it with $Al(NO_3)_3 \cdot 9H_2O$ solution (50 mmol) in 20mL of deionized water. The mixture was then combined with a sufficient volume of NH_4OH solution (20 wt%) until total precipitation was accomplished at a pH range

of 8-9. The isolated chemical was rinsed extensively with deionized water before drying. To obtain $ZnAl_2O_4$ nanoparticles, the dry product was calcined at 550 °C for 5 hours. The resulting compound was annealed at 800 °C to produce $ZnAl_2O_4$ nanoparticles.

3) Catalytic Hydrocracking Process

Hydrocracking reaction experiments for the prepared used cooking oil were carried out to investigate the impact of various operating conditions on the quality and quantity of products produced by a zinc aluminate nanoparticle catalyst or a Zeolite catalyst (ZNS-5) in a modest continuous high-pressure reactor unit [18]. The key operational parameters of hydro processing processes are the reaction temperature, hydrogen pressure, and feedstock liquid space velocity per hour. Each variable's influence on the process was explored while keeping the H_2/Oil ratio constant at 600 V/V and the other variables constant. The experimental variables examined were temperature, hydrogen pressure, and space velocity. For temperature, values of 350°C, 375°C, 400°C, 425°C, and 450°C were tested. Hydrogen pressures of 30, 50, and 70 bar were used. Finally, space velocities of 1, 2.5, and 2 liquid hours⁻¹ were evaluated.

Before the feedstock oil was pumped into the reactor, the reactor was flushed with hydrogen gas and kept under hydrogen gas pressure to check for leaks. The operating conditions in the hydro-conversion runs were adjusted as needed. Once the feed reached a steady state, it was pumped into the reactor. After the reaction, the reactor effluent was cooled in a water condenser and separated into liquid and gas phases.

The liquid product, which consisted of organic and aqueous fractions, was taken in and measured in a receiver. Meanwhile, the gases were directed to the outlet using a gas meter. The contaminated water from the liquid yield was removed after 24 hours of settling in a separating funnel. Anhydrous sodium sulfate was added to the organic product to remove any remaining water. The organic products and crude oils were analyzed and evaluated. The unconverted vegetable oil was separated from the organic product using an atmospheric distillation unit. The residue that remained after distillation was known as residual and/or unconverted oil. Furthermore, fractional distillation was used to separate the produced biofuel into three fractions based on their boiling points; biogasoline, light fraction of biogasoline (IBP–160 °C), biokerosene (160–270 °C), and biodiesel (270–350 °C) [19]. All of these products were estimated and characterized by various ASTM standards.

4) Product Separation

After the hydro-cracking reactor, the resulting mixture contains a wide range of hydrocarbon compounds with different boiling points. Fractional distillation is employed to separate these components based on their boiling points. The mixture is introduced into a fractional distillation column, which consists of a vertical tower with multiple trays or plates. The column is maintained at decreasing temperatures from bottom to top. The trays in the column allow for the separation of different fractions based on boiling points [20], [21]. The compounds with lower boiling points, such as lighter gases and gasoline-like components, collect at the top of the column, while heavier components like diesel, kerosene, and lubricants collect at

lower trays.

The atmospheric distillation technique specified in ASTM D-86 was used [22]. The volume % was computed at various (BP) boiling points ranging from 50 to 350 °C. A specific Equation (1) [23] was used to compute the yield of the distilled fractions as well as the bottom residual product.

$$\text{Disillation Fracion (wt. \%)} = \frac{\text{Mass of Distilled Fraction}}{\text{Mass of Organic Liquid Product}} \quad (1)$$

5) *Characterization of Zn Al₂O₄ Nano-Catalyst*

The physio-chemical characteristics of the catalysts were investigated using various analytical tools. These tools include Energy dispersive X-ray analysis (EDX), X-Ray Diffraction Analysis (XRD), Nitrogen Adsorption Measurements, Fourier Transform Infra-Red Spectroscopy (FTIR), Transmission Electron Microscope (TEM), and Scanning Electron Microscope (SEM) [22].

6) *Green Product Analysis*

The biodiesel and biojet fractions obtained from the atmospheric distillation process of the generated organic liquid were tested using various standard ASTM procedures.

7) *Green Fuel Blends Characterization*

Samples of green products were withdrawn after a fractional distillation stage in the jet fuel range (170-270 °C) and (270-350 °C) of the diesel fuel range and then the samples were blended with 50% of fossil jet -A and diesel fuel respectively. After that, tests were performed to verify that the properties of these B50 blends conform to the ASTM diesel fuel specifications.

3. Results and Discussion

A. *ZnAl₂O₄ Catalyst Characterization*

1) *Energy Dispersive X- Ray Analysis (EDX) ZnAl₂O₄*

This technique was used to quantify the mass fraction of each ingredient in the base ZnAl₂O₄ catalyst [24]. This procedure includes bombarding the studied specimen with electrons, generating a vacuum within the atoms of the material, then filling it with larger-energy electrons from the atoms' exterior [24]. The change of the more energetic electrons into less energy shells causes part of their energy to be emitted in the form of X-rays, with the quantity varying depending on the kind of atoms. As a consequence, adapting to its content in the sample under examination, each atom will have a separate peak with a specified altitude in the EDX spectrum. The prevalent EDX spectra acquired for the parental ZnAl₂O₄ particles are shown in Table 1 and Figure 1.

Table 1

Investigation of the EDX for the parental ZnAl₂O₄ nano-catalyst

Element	Weight %	Atomic %	Net Int.	Error %
O	26.84	49.13	101.12	10.11
Al	28.38	30.8	204.75	9.04
Zn	44.78	20.06	94.2	6

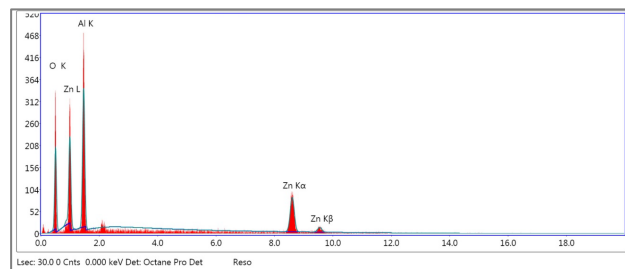


Fig. 1. The parental ZnAl₂O₄ catalyst's EDX band

2) *ZnAl₂O₄ Nano-Catalyst X-ray Diffractions (XRD) Investigation*

Figure 2 illustrates the X-rays diffractions profiles of the produced catalyst. This specimen formed a solitary phase with a spinel structure and space group Fd-3m. Based on (ICDD card No. 00-004-0160) [25], the primary section of spinel that referenced cubic phase of ZnAl₂O₄ particles configuration with color deep blue. The measured peak values of diffraction at 2θ are 36.79, 44.64, 55.52, 59.33, 65.25, 73.91, and 77.42 and can be attributed to the (220), (311), (400), (331), (422), (511), (440), (620), and (533) surfaces of ZnAl₂O₄.

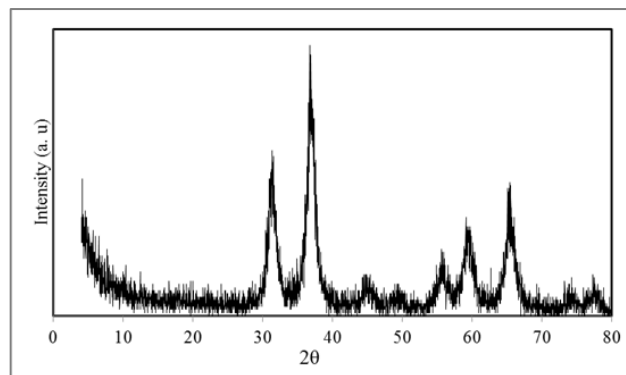


Fig. 2. X-Ray D analysis of a ZnAl₂O₄ nano-catalyst

3) *Isotherm of N₂ Adsorption and Desorption*

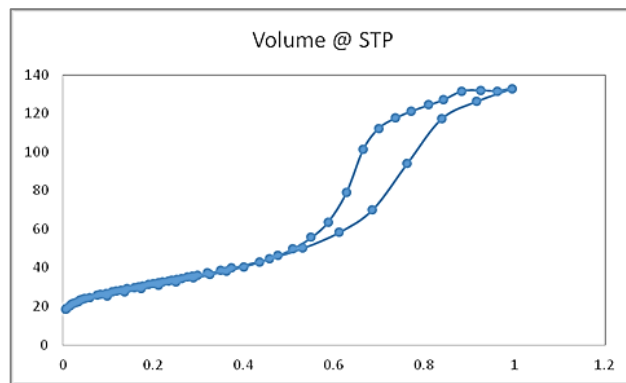


Fig. 3. N₂ adsorption-desorption isotherm of ZnAl₂O₄ catalyst

Figure 3 describes the nitrogen' adsorption/desorption isotherms' and pore size distributions of the tested samples. The adsorption isotherm has three separate parts: monolayer-multilayer adsorption, capillary condensation, and multiple layers of adsorption on the superficial particle surfaces. According to the -International Union of Pure and Applied

Chemistry- (IUPAC) the organization, the produced sample exhibits a type IV isotherm [27]. The $ZnAl_2O_4$ particles has a BET surface area of $113 \text{ m}^2\text{g}^{-1}$, a pore width of 6.8 nm, and a volume of pore of $0.3 \text{ cm}^3 \text{ g}^{-1}$ according to the values in Table 2.

Table 2
Morphological description of $ZnAl_2O_4$ nano-catalyst

Catalyst	SSA/ m^2/g	Pores	Pore Sizer
		Diameter/nm	Distributions/ccg
$ZnAl_2O_4$	112.854	7.29	0.205

4) $ZnAl_2O_4$ Nano-Catalyst Infrared Spectroscopy using the Fourier Trans (FTIR)

Figure 6 represents the FT-IR spectra of $ZnAl_2O_4$. The OH group stretching vibrations of water molecules produce a large band about 3600 cm^{-1} and a narrow band near 1700 cm^{-1} in the spectrum. The FT-IR spectra of $ZnAl_2O_4$ nano-catalyst formed by calcined the precursor at 700 C for 5 h reveals two prominent bands beneath 1000 cm^{-1} about 630 and 565 cm^{-1} . These bands correspond to the Al-O stretching group and O-Al-O bending vibrations of AlO 6 groups in the spinel-type $ZnAl_2O_4$ configuration [27], [28]. The quantity and form of $ZnAl_2O_4$ and FT-IR bands are determined by the technique of production. It should be noticed that this result matches with the XRD test findings. In the range of ($450\text{--}700\text{cm}^{-1}$), $ZnAl_2O_4$ shows two or three bands.

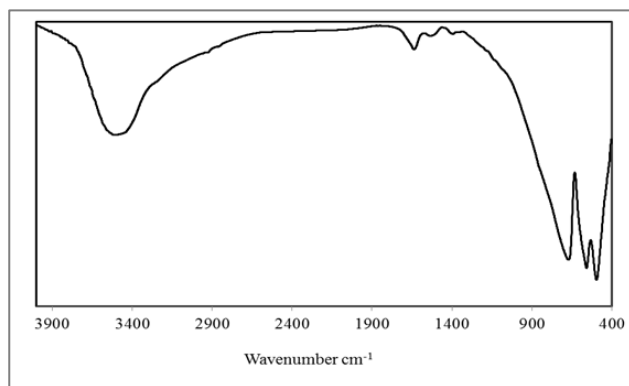


Fig. 4. FT-IR inspection of $ZnAl_2O_4$ nano-catalyst

5) $ZnAl_2O_4$ Nano-Catalyst High Resolution Transition Electron Microscopy (HRTEM)

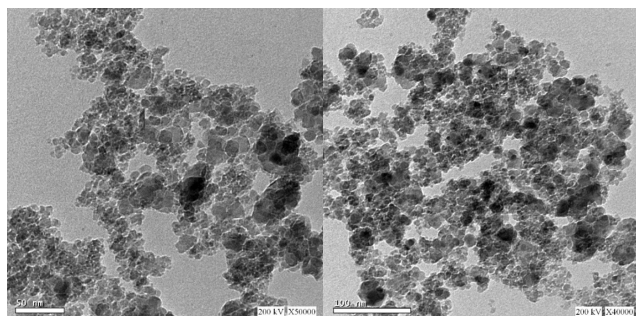


Fig. 5. HRTEM of $ZnAl_2O_4$ investigation

From the Figure 5, it is shown that the synthesized particles are homogeneous and nanoaggregate, with dimensions of particles less than 50 nm in the $ZnAl_2O_4$ specimen transmitted images.

6) $ZnAl_2O_4$ Nano-Catalyst SEM (Scanning Electron Microscope)

HR-SEM was employed to investigate the form and morphological concepts of the surface of $ZnAl_2O_4$ nanoparticles. The HR-SEM images of untainted zinc aluminate nano-catalyst were found to be homogenous, with grains dispersed evenly, as illustrated in Figure 6. The particle size varies from 18.94 to 21.74 nm and 25.22 nm, with negligible aggregation, according to the SEM pictures.

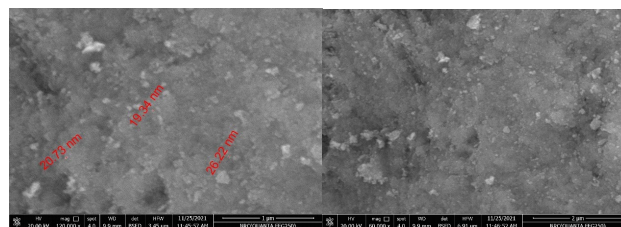


Fig. 6.

B. Effect of Hydrocracking Process Temperature

The cracking process was carried out using synthesized $ZnAl_2O_4$ nano catalyst at different temperatures of 350, 400, and 450 °C. After that, the resultant liquid effluent was subjected to fractional distillation in the atmosphere. which resulted in three principal fractions: green gasoline ($70\text{--}170 \text{ }^\circ\text{C}$), green kerosene ($170\text{--}270 \text{ }^\circ\text{C}$), and green diesel ($270\text{--}350 \text{ }^\circ\text{C}$). It has been observed that the distillation temperature intervals create fractional amounts of hydrocarbon with properties similar to certain petroleum products [29]. The conversion rate as well as yield of each produced segment from the distillation step were discovered to be affected by reaction temperature. Used cooking oil was predicted to first fracture thermally and catalytically on the catalyst's outer surface, forming heavy hydrocarbons and oxygen, preceding cracking within the $ZnAl_2O_4$ inner pore structure, yielding light alkenes, alkanes, water, carbon dioxide, and carbon monoxide [30].

various reactions may prevail in the nano molecules at diverse reaction temperatures, which may help elucidate how Temperature has an impact on conversion. Table 3 illustrates that as the process temperature rises owing to the quicker rate of cracking, the conversion of utilized cooking oil increases steadily. At 450°C and 50 bar of pressure of hydrogen, and 1 h^{-1} , the highest conversion rate of 95 weight percent was achieved. Similar patterns had previously demonstrated the same conclusions [30], [31]. In general, as the reaction temperature increased, the yield of the light and biokerosene fractions increased; the maximum yield of biokerosene approached 30%, while the best yield of biodiesel resulted at $400 \text{ }^\circ\text{C}$ in a comparable LHSV of 1 h^{-1} , as indicated in Table 3.

Table 3

The influence of reaction temperatures on oil conversions over ZnAl₂O₄ nano-catalyst. (1 h⁻¹, LHSV: 50 bar) (50 bar, LHSV: 1 h⁻¹)

Temperature °C	350	400	450
'Oil Liquid Product' %			
Light Fraction (Gasoline) (IBP-170°C)	14	11	28
Biokerosene Fraction (170-270°C)	10	19	30
Biodiesel (270-340°C)	13	48	28
Residue (>350 °C)	60	17	5
Water%	3	6	9
Conversion %	85	90	95

C. Effect of Hydrocracking Hydrogen Pressure

Another crucial component in the hydrogenation process procedure is pressure of hydrogen pressure. Higher hydrogen pressure is needed to increase the output of the hydrodeoxygenation, process, which produces hydrocarbons. This investigation includes multiple pressure tests at three distinct pressures, namely 30 bar, 50 bar, and 70 bar Table 4. The hydrotreatment of used cooking oil 'feedstocks' has confirmed that levitation the pressure of hydrogen in the system increases the overall level of hydrogen in the liquid mixture, hence preferring hydrogenation and hydrogenolysis processes [32]. Furthermore, because hydrogen is necessary to remove the oxygen atom in the hydrodeoxygenation and decarbonylation processes, increasing the temperature can help render hydrogen more readily soluble in the liquid mixture. As pressure increased to 70 bar, the yield of the green diesel fuel range in the liquid product reduced, but the yield of the light proportion and the biokerosene range elevated. While increased hydrocracking pressures typically aid in increasing conversion to an ideal level, very high pressures can be counterproductive and actually reduce conversion. This is due to the fact that at very high pressures above the ideal threshold, undesired secondary cracking processes are accelerated, resulting in the breakdown of useful fuels into smaller hydrocarbons and a reduction in yields [33]. Additionally, excessively high pressures might deteriorate the catalyst over time, resulting in non-selective cracking on damaged sites and decreased conversion to desirable products [33], [34]. High pressure can also condense the catalyst bed, decreasing the overall reaction rate and conversion. Furthermore, because hydrocracking is reversible, very high pressures shift equilibrium towards reactants, coke production increases, which clogs catalytic sites, and probable supercritical phase shifts negatively affect mixing and kinetics, all of which reduce conversion as noticed in Table 4 where the conversion reached 82% when the pressure was 70 bar. While increasing pressure aids conversion to a point, excessive pressures cause secondary reactions, catalyst degradation, mass transfer difficulties, thermodynamic equilibrium shifts, coking, and fluid phase changes. To optimize hydrocracking conversion, precise pressure control is required [35].

Table 4

The influence of operating pressure on oil hydro-conversion over ZnAl₂O₄ nano-catalyst. (400 °C, LHSV: 1 h⁻¹)

Pressure (bar)	30	50	70
'Oil Liquid Product' %			
Light Fraction (Gasoline) (IBP-170°C)	8	15	19
Biokerosene Fraction (170-270°C)	10	13	20
Biodiesel (270-350°C)	13	59	46
Residue (>350 °C)	67	13	15
Water%	7	6	7
Conversion %	87	90	82

D. Liquid Hourly Space Velocity Effect

The LHSV is a critical operational component for sustaining catalyst lifespan and functioning because it governs the frequency of feed into the catalyst [36]. The three distinct LHSV levels evaluated were 1, 1.5, and 2 h⁻¹. Table 5 summarizes the hydrocracking product variations of organic liquids. The largest conversion had taken place at LHSV_s of 1 h⁻¹ at 400 °C and 50 bars of hydrogen pressure, according to the table, whilst the conversion reduction in as space velocity increased to 1.5 and 2 h⁻¹, which is in line with previous studies [35,36]. The higher LHSV may minimize cracking reactions. As LHSV grew, the simple light fraction hydrocarbon yield reduced, while the biokerosene and biodiesel fraction yields increased. This might imply that hydrodeoxygenation and, as a result, cracking of normal paraffin was not observed at higher LHSV_s due to insufficient residence time. By preventing cracking, enhancing the LHSV can result in increased kerosene/diesel fraction output Table 5. This observation appears to corroborate prior findings [37].

Table 5

The influence of oil's liquid hourly space velocity on ZnAl₂O₄ nano-catalyst. (Temperature 400 °C, Pressure 50 bar)

LHSV (h ⁻¹)	1	1.5	2
'Oil Liquid Product' %			
Light Fraction (Gasoline) (IBP-170°C)	18	14	11
Biokerosene Fraction (170-270°C)	19	15	22
Biodiesel (270-350°C)	48	58	55
Residue (>350 °C)	15	13	12
Water%	6	11	6
Conversion %	90	86	84

Reliance on the outcomes of Tables 3, 4, and 5, the most effective situations for producing a substantial amount of light products with a hydrocarbon amount of 18% (green gasoline) and a significant yield of 19% green kerosene and 48% green diesel fuel portions in this investigation were 400°C, 50 bar, and 1 LHSV_s (h⁻¹).

E. Comparative Performance of ZnAl₂O₄ and Zeolite (ZSM-5) Catalysts in Used Cooking Oil Hydrocracking

Table 6 provides data on the percentage of different products obtained from the hydrocracking of used cooking oil using two different catalysts, ZnAl₂O₄ Nano-Catalyst and Zeolite (ZSM-

5), under optimal conditions. The results show that the ZnAl₂O₄ Nano-Catalyst was more effective in producing biodiesel, with a yield of 48%, compared to only 20% with Zeolite (ZSM-5). On the other hand, Zeolite (ZSM-5) was more effective in producing the biokerosene fraction, with a yield of 24%, compared to only 19% with ZnAl₂O₄ Nano-Catalyst. The light fraction (gasoline) was produced in similar amounts using both catalysts, with yields of 18% and 19% for ZnAl₂O₄ Nano-Catalyst and Zeolite (ZSM-5), respectively. The residue, which is the least desirable product, was produced in higher amounts using ZnAl₂O₄ Nano-Catalyst, with a yield of 15%, compared to only 1% with Zeolite (ZSM-5). Overall, the results suggest that ZnAl₂O₄ Nano-Catalyst is a more effective catalyst for producing biodiesel from used cooking oil, while Zeolite (ZSM-5) is more effective for producing the biokerosene fraction.

Table 6

ZnAl₂O₄ Nano-Catalyst Vs. Zeolite (ZSM-5) for Hydrocracking of used cooking oil at the optimum conditions

Oil Liquid Product %	ZnAl ₂ O ₄	Zeolite (ZSM-5)
Light Fraction (Gasoline) (IBP-170°C)	18	55
Biokerosene Fraction (170-270°C)	19	24
Biodiesel (270-350°C)	48	20
Residue (>350 °C)	15	1
Water %	6	8
Conversion %	90	97

Table 7

Physicochemical properties of green fuels in biokerosene range (170-270 °C) produced by hydrocracking of used cooking oil using ZnAl₂O₄ and ZSM-5 catalysts

Test	Standard Test Method [39,40]	ZnAl ₂ O ₄	ZSM-5
Density @ 15 °C; (g/cm ³)	ASTMD-4052	0.8327	0.8304
Flash point °C	IP 170	44	42
Gum content mg/100ml	ASTMD381	4.4	4
Sulphur ppm	ASTMD5453	<0.5	<0.5
Freezing point °C	ASTMD 7153	-75	-80

Table 7 shows the physicochemical properties of green fuels in the range of biokerosene fraction (170-270 °C) produced by hydrocracking of used cooking oil using ZnAl₂O₄ and ZSM-5 catalysts. The properties tested include density, flash point, gum content, sulfur content, and freezing point. The results show that the green fuels produced by both catalysts have similar densities, but the flash point and gum content of the fuels produced by ZnAl₂O₄ are slightly higher than those produced by ZSM-5. The sulfur content of the fuels produced by both catalysts is very low, and the freezing point of the fuels produced by ZSM-5 is slightly lower than those produced by ZnAl₂O₄.

Table 8

Physicochemical properties of green fuels in diesel range. produced by hydrocracking of used cooking oil using ZnAl₂O₄ and ZSM-5 catalysts

Properties	Standard Test Methods [39,40]	ZnAl ₂ O ₄	ZSM-5
Density @ 15 °C; (g/cm ³)	ASTMD-4052	0.8491	0.8491
Sulfur content; (%wt)	ASTMD-5453	0.0017	0.0016
Flash point (P.M.C.C); (°C)	ASTMD-93	60	62
Pour point; (°C)	ASTMD-97	3	0
Kinematic viscosity @ 40 °C; (cSt)	ASTMD-445	5.243	5.134
Water and sediment content; (%Vol.)	ASTMD-2709	Nil	Nil
Copper Corrosion strip @ 50 °C/3 hrs	ASTMD-130	1A	1A

Table 9

Physical properties of biodiesel fraction range blends with 50% fossil diesel' fuel's for ZnAl₂O₄ and ZSM-5 catalyst

Properties	B50" (50% Green Biodiesel + 50% Fossil Oil Fuel) Zn-Al ₂ O ₄	B50" (50% Green Biodiesel + 50% Fossil Oil Fuel) ZSM-5	Fossil Oil Fuel	Specification Limits	Standard Test Method [39,40]
Density @ 15 °C; (g/cm ³)	0.8260	0.8235	0.8206	Reported	ASTM D-4052
Flash point (P.M.C.C); (°C)	84	83	109	52 (min.)	ASTM D-93
Pour point; (°C)	0	-0	-9	15 (max.)	ASTM D-97
Cloud point; (°C)	15	9	3	Reported	ASTM D-2500
Kinematic viscosity at 40 °C; (cSt)	4.786	4.6521	3.96	1.6 - 7	ASTM D-445
Distilled @ 350 °C; (%vol)	90	92	90	85 (min.)	ASTM D-86
Water and sediment content; (%vol)	Nil	Nil	Nil	0.1 (max.)	ASTM D-2709
Sulfur content; (%wt)	0.0048	0.0045	0.006	1 (max.)	ASTM D-4294
Copper Corrosion strip @ 50 °C/3 hrs	1A	1A	1A	1 (max.)	ASTM D-130
Carbon residue; (%wt)	0.072	0.071	0.07	0.1 (max.)	ASTM D-4530
Ash content; (%wt)	Nil	Nil	Nil	0.01 (max.)	ASTM D-482
Colour	1	1	0.5	4 (max.)	ASTM D-6045
Cetane index	54.5	54.6	55	46 (min.)	ASTM D-4737
Aniline point; (°C)	68	66	70	Reported	ASTM D-611

The physicochemical parameters of green fuels in the range of diesel (270-350 °C) generated by hydrocracking used cooking oil with ZnAl₂O₄ and ZSM-5 catalysts are shown in Table 8. Density, Sulphur content, flash point, pour point, kinematic viscosity, sediment content, water and copper corrosion strip were all examined. The outcomes reveal that both catalysts create green fuels with equal densities, Sulphur content, and flash point. The fuels generated by ZSM-5, on the other hand, have a lower pour point and kinematic viscosity

than those produced by ZnAl_2O_4 . Furthermore, both catalysts provide green fuels with no water or silt content, as well as no copper corrosion strip.

The physical properties of biodiesel blends produced from the 270-350°C fraction using ZnAl_2O_4 and ZSM-5 catalysts were tested, Table 9. Blends were made with 50% fossil diesel fuel. Tested properties included density, flash point, pour point, cloud point, and kinematic viscosity. The biodiesel blends from both catalysts had similar densities, flash points, and pour points. However, biodiesel from ZSM-5 catalyst had a lower cloud point and slightly lower viscosity compared to ZnAl_2O_4 . The properties were compared to fossil oil fuel specifications. Both catalyst biodiesel blends met limits for density, flash point, pour point, and viscosity. But the cloud point of ZnAl_2O_4 biodiesel blend exceeded specifications slightly. Overall, biodiesel from both catalysts had comparable physical properties meeting most fuel specifications, but ZSM-5 biodiesel had a slight advantage in cloud point and viscosity.

4. Conclusion

Using a co-precipitation technique, this work effectively synthesized zinc aluminate (ZnAl_2O_4) nano-catalyst. The ZnAl_2O_4 catalyst has a high surface area of 112 m^2/g and homogeneous sub-50 nm particles, as determined by XRD, SEM, TEM, FTIR, and N_2 physisorption. The hydrocracking of used cooking oil over ZnAl_2O_4 nanoparticles was performed at variable temperatures (350-450°C), hydrogen pressure (30-70 bar), and space velocity ($1-2 \text{ h}^{-1}$). Oil conversion increased with increasing temperature and pressure until it reached an ideal value due to higher cracking reaction rates. At 400°C, 50 bar H_2 pressure, and 1 h^{-1} space velocity, the ZnAl_2O_4 catalyst performed best, yielding 18% biogasoline, 19% biokerosene, and 48% biodiesel. Increasing the space velocity was counterproductive and reduced conversion due to insufficient dwell time. ZnAl_2O_4 nanoparticles outperformed ZSM-5 zeolite in terms of catalytic activity and selectivity for hydrocracking processes, favoring biodiesel range hydrocarbon synthesis. When evaluated, the biokerosene and biodiesel fractions produced from ZnAl_2O_4 hydrocracking fulfilled the majority of the essential fuel property standards. Because of their high activity, selectivity, and stability, zinc aluminate nano-catalysts have emerged as attractive hydrocracking catalysts for green fuel production from vegetable oils. This research contributes to the development of ZnAl_2O_4 catalysts and the optimization of hydrocracking process parameters for the production of sustainable transportation fuels.

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