CATALYTIC PERFORMANCE OF WASTE WOOD ASH IN THE METHANOLYSIS OF SUNFLOWER OIL

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Biomass combustion waste ash, such as wood ash, represents a promising low-cost raw material for the biodiesel industry, as it predominantly consists of alkali and alkaline earth metal oxides. In this study, biodiesel production from sunflower oil via methanolysis was investigated using waste wood ash as a catalyst. This is the first study to integrate detailed physicochemical characterization, catalytic performance evaluation, and a preliminary economic assessment for the valorization of waste wood ash as a catalyst in sunflower oil methanolysis. The catalyst was comprehensively characterized to determine its thermal behavior, chemical and phase composition, textural properties, morphology, and base strength. The catalyst composition indicated Ca (43 wt.%) and K (18 wt.%) as the major elements, consistent with the XRD results, which identified their oxides as dominant phases. The catalytic performance of wood ash was evaluated under atmospheric pressure in batch mode. The influence of catalyst loading (5-15 wt.%, based on the oil mass) and methanol-to-oil molar ratio (9:1-15:1) on the fatty acid methyl esters (FAMEs) content was investigated at a reaction temperature of 60 °C. The rapid conversion of triacylglycerol (TAG) into FAME was observed, indicating negligible TAG mass transfer limitations. Increasing catalyst loading significantly enhanced FAME formation with 15 wt.% as the optimal value within the investigated range. While the methanol-to-oil molar ratio had a slight positive effect on the final FAME content, higher ratios reduced the reaction time required to achieve FAME contents above 95% from 40 to 20 min at the highest catalyst loading. Despite the high feedstock cost indicated by preliminary cost analysis, the results demonstrated that waste wood ash is an effective low-cost catalyst for biodiesel production, although its catalytic activity is limited to a single reaction cycle.

Keywords: biodiesel, heterogeneous catalysis, waste valorization, wood ash

Introduction

The extensive use of fossil fuels as the primary energy source has led to significant adverse effects on climate change, the environment, natural resources contamination, energy security, and human health. With rapid economic and technological development, global energy demand continues to rise, further intensifying fossil fuel consumption. Within the European Union, the transport sector remains the dominant energy consumer, accounting for approximately 31% of the total energy consumption in 2022, exceeding that of households (27%) and industry (25%). Road transport alone represented 74% of total energy consumption in the transport sector, with fossil fuels contributing 90.6% of this demand [1]. At the global level, CO_2 emissions from fossil fuel combustion increased by approximately 1% in 2024, despite a 2.3% decline in emissions from industrial processes [2]. Passenger cars are a major contributor, responsible for nearly 61% of total CO_2 emissions from EU road transport. Consequently, reducing CO_2 emissions and dependence on fossil fuels has become a critical priority, driving the search for renewable and sustainable fuel alternatives.

Among the available alternatives, biodiesel has emerged as a promising renewable fuel for the road transport sector due to its compatibility with existing diesel engines [3] and its substantial potential for reducing life-cycle greenhouse gas emissions compared with fossil diesel [4].

Biodiesel, typically a mixture of fatty acid methyl esters (FAME), is primarily produced through the catalyzed transesterification of triacylglycerols (TAG) from renewable feedstocks such as vegetable oils or animal fats with short-chain alcohols (commonly methanol). However, large-scale commercialization of biodiesel remains con-

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strained by relatively high production costs, which are strongly influenced by feedstock availability and catalyst selection.

Conventional biodiesel production predominantly relies on homogeneously catalyzed processes, most commonly using KOH and NaOH. Although these catalysts provide a high FAME yield under mild reaction conditions, their solubility in the reaction mixture promotes soap formation when oils with high free fatty acid (FFA) are used, causes wastewater contamination, and complicates catalyst separation and reuse [5]. Overcoming these limitations can be achieved by employing heterogeneous catalysts, which can be easily separated from the reaction mixture and regenerated for reuse [3]. Among heterogeneous catalysts, CaO has attracted considerable attention due to its low cost, high basicity, and widespread availability [6]. Moreover, it can be derived from waste natural materials, contributing to waste valorization, environmental protection, and reduced biodiesel production costs. Waste-derived CaO sources include chicken eggshells [7], shells of mussels, cockles, and scallops [8], plum stones [9], palm kernel shell biochar [10], waste filter cake from a sugar beet processing plant [11], and biomass wood ash [12, 13].

Wood ash is an inorganic, alkaline solid waste residue generated during wood combustion. With the ongoing transition from fossil to renewable energy sources, the generation of wood ash has increased, with the average ash yield produced during wood burning, ranging from 6-10 wt.% [14]. The physicochemical properties of wood ash strongly depend on the type of biomass and combustion conditions, necessitating comprehensive characterization to assess its potential applications. Chemical composition is commonly determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES), X-ray fluorescence (XRF), or energy dispersive spectroscopy (EDS); while phase composition is typically analyzed by X-ray diffraction (XRD), morphology by scanning electron microscopy (SEM), and textural properties by mercury porosimetry and nitrogen physisorption [15]. Wood ash has been investigated for diverse applications, including use as a soil amendment or fertilizer [14], a cement replacement in concrete [16], as a catalyst in gasification processes [17], a catalyst for benzochromene derivatives [18], and biodiesel production [12].

Despite its wide applications, wood ash is underutilized and is generally disposed of as waste. Its chemical composition varies with wood type, but typically includes oxides of Ca, K, as well as Si, Mg, and P [19], indicating its potential as a heterogeneous base catalyst for alcoholysis of TAG-rich feedstocks. This composition was the key factor in selecting wood ash as a catalyst, together with its heterogeneous nature, which enables easy separation from the reaction mixture. Moreover, its utilization represents a low-cost alternative to synthetically prepared catalysts and promotes the valorization of abundant waste material, which is in alignment with circular economy principles. Sharma et al. [12] demonstrated that while uncalcined wood ash exhibited limited catalytic activity in the methanolysis of jatropha oil (38.7% FAME yield), calcination at 800 °C significantly enhanced catalytic performance, resulting in a maximum FAME content of 97.7% under optimized reaction conditions. Similarly, Uprety et al. (2016) [3] evaluated the catalytic activity of birch bark ash, calcined at 800 °C for 4 h, in the methanolysis of palm oil. Under the same catalyst loading, methanol-to-oil molar ratio, and reaction time as those reported by Sharma et al. [12], but at 60 °C, birch bark ash achieved a FAME content of 88.06%. Adepoju et al. [20] further improved ash-based catalysts by calcining a mixture of wood ash, eggshell, and snail shell, which was used in the methanolysis of a ternary oil mixture (dika nut, palm kernel, and ukpaka). A FAME content of 98% was achieved under optimized reaction conditions, with the catalyst retaining catalytic activity for up to three reuse cycles.

This study focuses on FAME production from sunflower oil over waste wood ash as a sustainable catalyst. The aim of this study was to evaluate the physicochemical and textural characteristics of wood ash and to assess its catalytic performance in the methanolysis reaction. The wood ash was first characterized in terms of its thermal behavior, chemical and phase composition, morphology and textural properties, and base strength. Catalytic performance was subsequently evaluated under batch conditions, with particular emphasis on the effects of catalyst loading and methanol-to-oil molar ratio on FAME content. In addition, the catalyst reusability was tested, and the cost assessment was performed to identify the key factors influencing economic viability.

Materials and methods

Materials

Sunflower oil (Dijamant, Zrenjanin, Serbia) was purchased from a local store. Wood ash, obtained by burning wood in a solid fuel stove, was collected from a local household in Žitorađa, Serbia. The ash was stored in a closed container in a desiccator prior to the reaction. For the experimental work, the following reagents were used: *n*-hexane (HPLC grade; Lab-Scan, Ireland), methanol (99.5%; Zorka-Pharma, Serbia), methanol (HPLC grade; Promochem LGC, Germany), and 2-propanol (HPLC grade; Carlo Erba, Italy).

Catalyst characterization

The chemical composition of the wood ash was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using the Thermo Scientific iCAP-6300 Duo ICP-OES Analyzer (Thermo Fisher, UK) after acid digestion of the samples, and the results were expressed in wt.%. The crystalline phases in wood ash were identified by X-ray diffraction (XRD) using a Philips PW 1050 X-ray powder diffractometer with Cu $K\alpha_{1,2}$ radiation (λ=1.54178 Å), operating in a 2Θ range of 10-90°

with a step length of 0.01° and a scan time of 5 s. The simultaneous TGA-DSC analysis (Setsys, SETARAM Instrumentation, Caluire, France) was performed under a synthetic air atmosphere. Measurements were conducted from ambient temperature to 1200 °C at a heating rate of 20 °C/min, using an alumina sample pan. The textural properties of the catalyst were determined by Hg intrusion porosimetry and N_2 physisorption at 77 K. The bulk density was measured on a Macropore Unit 120 (Fisons Instruments) using mercury as the displacing fluid. The total intruded Hg volume, apparent density, and porosity were calculated using SOLver software version 1.3.4 after measuring Hg-intrusion with a Pascal 440 device (Thermo Electron) in the pressure range from 1 to 2000 bar. Nitrogen adsorption-desorption isotherms were recorded at 77 K on a Sorptomatic 1990 (Thermo Finnigan). The specific surface area was calculated by applying the Brunauer-Emmett-Teller (BET) equation [21], the micropore volume by the Dubinin-Radushkevich method [22], and the mesopore volume and the mesopore size distribution by the Barrett, Joyner, and Halenda (BJH) method [23]. Experimental procedure for Hg intrusion porosimetry and N_2 physisorption are described in detail elsewhere [24]. Morphological characterization of wood ash samples was performed using a Jeol JSM-5800 scanning electron microscope (SEM). The base strength and basicity of the wood ash were determined by the Hammett indicator method, using phenolphthalein (H_=9.3), thymolphthalein (H_=10.0), thymol violet (H_=11.0), and 2,4-dinitroaniline (H_=15.0).

The methanolysis procedure

The methanolysis reaction of sunflower oil catalyzed by wood ash was conducted in a stirred batch reactor (900 rpm) at atmospheric pressure and a reaction temperature of 60 °C. To evaluate its catalytic performance, the influence of catalyst loadings (5-15 wt.%, based on the oil mass) and methanol-to-oil molar ratios (9:1-15:1) on the FAME content was investigated. First, the required masses of methanol and catalyst were mixed at 400 rpm and thermostated at the target reaction temperature for 30 min. The reaction was then initiated by adding the prethermostated sunflower oil (30 g). During the reaction, aliquots (0.5 mL) of the reaction mixture were withdrawn at defined time intervals and centrifuged at 3500 rpm (Sigma centrifuge, type 2-6E Germany) for 10 min to separate the ester-oil, methanol-glycerol and catalyst phases. Finally, the upper ester-oil layer was dissolved in a mixture of 2-propanol:*n*-hexane (5:4 v/v) in a ratio of 1:200, filtered through a Millipore (0.45 μm) filter and analyzed by high-performance liquid chromatography (HPLC) [25]. The experiments were performed in duplicate.

Results and discussion

Wood ash characterization

The thermal behavior of the wood ash sample (Figure 1) was investigated using simultaneous TGA–DSC measurements in the temperature range from ambient temperature up to 1200 °C. The TGA curve indicated a minor initial weight loss (1.7%) below 400 °C, corresponding to the removal of moisture and low-molecular weight volatile compounds remaining after the initial combustion of the wood [24]. A small weight loss (of about 1%) observed in the 400-430 °C temperature range could be attributed to the dehydroxylation of mineral phases such as portlandite, or to the oxidation of trace amounts of residual carbon present in the ash [26]. The most pronounced weight loss occurred in the temperature interval 600-840 °C with a distinct peak near 780 °C and a strong accompanying endothermic effect. This dominant weight loss step is attributed to the thermal decomposition of carbonate phases, primarily calcium carbonate [26, 27]. A small weight loss at higher temperatures (above 850 °C) could be attributed to the evaporation of KCl [27]. Finally, at temperatures above 1100 °C, the TGA curve approaches a plateau, indicating the formation of thermally stable inorganic residues, such as oxides and silicate phases. The overall weight loss across the entire heating range is approximately 25%. This is consistent with the reported value of 27% for wood ash generated under uncontrolled burning of wood biomass [28].

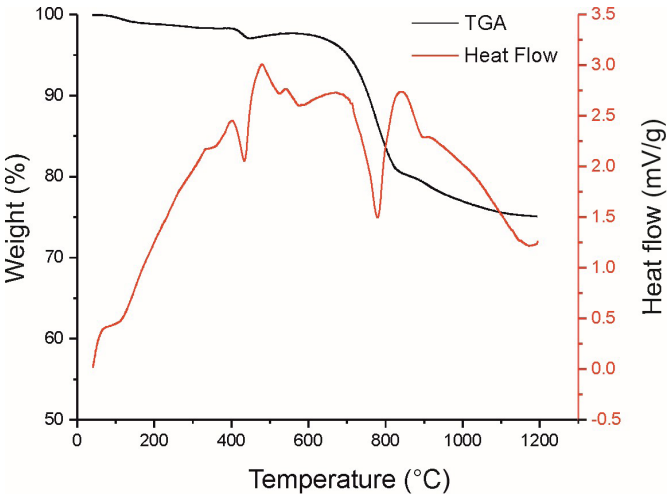

Figure 1. TGA-DSC profile of wood ash

According to ICP-OES analysis, the major constituent elements in the wood ash were Ca (43.0%) and K (18.0%), followed by Mg (4.3%) and Si (3.1%), whereas Al (0.75%), Na (0.58%), Mn (0.23%), and Fe (1.27%) were present in lower amounts. Lower contents of Ca (14.7%) and K (7.3%) were reported for *Acacia nilotica* wood ash, and the content of Ca increased to 36.6% with increasing calcination temperature of wood ash [12]. To elucidate the mineralogical forms in which these elements occurred, XRD analysis was performed. The crystalline phases in wood ash identified by XRD are presented in Figure 2. The diffraction peaks indicated the presence of CaO, $CaCO_3$, SiO_2, K_2O, and MgO phases. In particular, the peaks at 32.4, 37.6, 54.2, 64.4, and 67.6° correspond to the CaO phase, which was the predomi-

nant crystalline phase, followed by $CaCO_3$ identified at 29.58, 36.0, 39.8, 43.4, 47.7, and 48.7°. The occurrence of $CaCO_3$ resulted primarily from reactions between combustion-released CO_2 and Ca oxyhydroxides formed during organic matter decomposition and oxidation [29]. $CaCO_3$ commonly appeared as a result of combustion at temperatures ranging from 400 °C to 700 °C [30]. In addition, $CaCO_3$ has been detected in woody biomass bottom and fly ash collected from a biomass power plant [31-33]. Peaks at about 23.8, 27.8, 39.6, 48.0, and 64.7° suggested the presence of K-containing crystalline phases reported as K_2O equivalents. However, these positions may overlap with SiO_2, as well as with Na_2O, $CaCO_3$ and CaO phases. Additionally, the diffraction peaks at around 43.4 and 47° indicated the presence of MgO. The similar phase composition of wood ash was reported by Smołka Danielowska and Jabłońska [34]. The CaO, SiO_2, K_2O and MgO phases were identified in walnut shell ash [24], while the CaO, SiO_2 and $CaCO_3$ phases were detected in the ash of the *Acacia nilotica* tree [12]. Also, the dominant crystalline phase of CaO was found in non-woody ashes such as indigofera leaves ash [13].

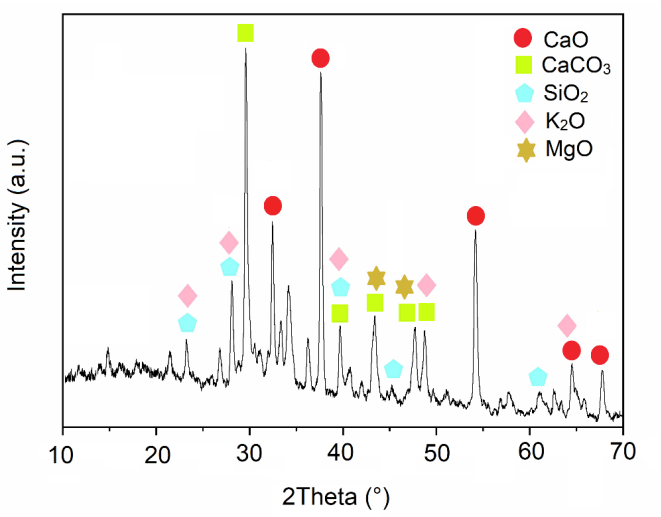

Figure 2. XRD patterns of wood ash

The textural properties of wood ash, determined by Hg porosimetry and N_2 physisorption, are summarized in Table 1. Additionally, the total Hg intrusion volume and the corresponding pore size distribution (PSD) obtained from two consecutive measurements (Run 1 and Run 2) are presented in Figure 3. The Hg intrusion curve in the first run (Run 1) revealed a substantial total pore volume of approximately 0.9 cm^3/g, indicating a highly porous structure of the wood ash sample. A sharp increase in the cumulative intrusion volume was observed in the pore diameter range of 3-10 μm. Although this may correspond to a dominant pore population, as suggested by the broad maxima in the PSD curve, it could also originate from mercury penetration into interparticle voids in loosely packed powder. This phenomenon does not necessarily represent the intrinsic porosity of the ash but rather reflects the stochastic arrangement of weakly bound agglomerates formed during the sample loading into the dilatometer (sample holder). To distinguish interparticle and intraparticle contributions, a second intrusion cycle (Run 2) was conducted following the initial Hg intrusion-extrusion process (Run 1). The intrusion profile obtained in Run 2 shows an almost identical distribution to Run 1 (Figure 3). However, the total cumulative volume at maximum pressure was reduced by approximately 17%, resulting in a still substantial value of 0.74 cm^3/g (Table 1). This reduction indicated that interparticle voids account for less than one-sixth of the total volume measured in Run 1, provided that mercury was successfully withdrawn from the interparticle spaces during the first extrusion. Consequently, the high intrusion volume recorded in Run 1 can be attributed to intraparticle porosity, representing the actual pore system inherent to the wood ash particles. The dominant pore system, characterized by modal pore diameters of 4.33 μm for Run 1 and 4.26 μm for Run 2, along with a minor volume increase in the mesopore region (D≤50 nm), indicates that the wood ash is predominantly a macroporous material. This characteristic, along with a high porosity of 58.5% measured in Run 2, is generally considered advantageous for heterogeneous catalytic applications, particularly regarding the efficient mass transport of reactants and products.

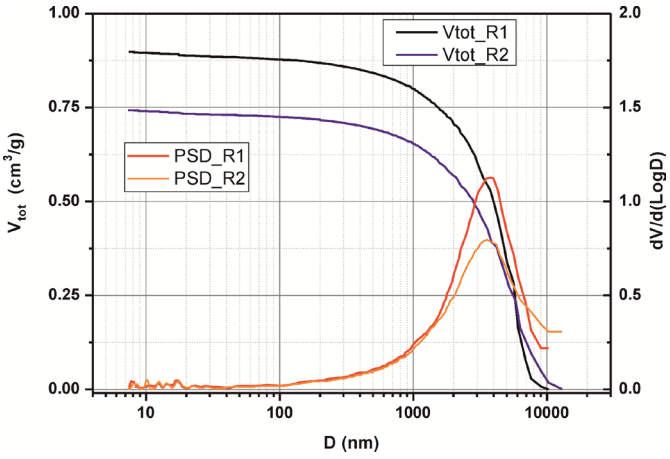

Figure 3. Total intruded Hg volume and pore size distribution of wood ash for two consecutive runs

To overcome the technical limitations of Hg porosimetry in fully characterizing the textural properties of wood ash, particularly the inability to detect pores smaller than 7.5 nm at the maximum applied pressure of 2000 bar and the potential influence of sample compaction on pore formation or collapse, further characterization was performed using nitrogen physisorption at 77 K. Although the total nitrogen uptake is relatively low, the adsorption-desorption isotherm exhibits a plateau at relative pressures near 0.9 and a pronounced hysteresis loop (Figure 4). These features are characteristic of a Type IV isotherm according to the IUPAC classification [35], which is typical for mesoporous materials. Similar Type IV behavior has

Table 1. Textural properties of wood ash obtained by Hg-porosimetry and N_2 physisorption

	Hg porosimetry					N_2 physisorption at 77 K		
	Total intruded Hg volume[a], cm^3/g	Apparent density, g/cm^3	Bulk density[b], g/cm^3	Specific surface area (Hg)[c], m^2/g	Porosity, %	Mesopore volume, cm^3/g	Micropore volume, cm^3/g	Specific surface area, m^2/g
Run 1	0.898	1.896	0.702	5.8	63.0	0.045	0.006	14.5
Run 2	0.743	1.896	0.787	5.2	58.5			

[a] at 200 MPa,
[b] at atmospheric pressure,
[c] for cylindrical and plate pore model.

been reported for biomass fly ash derived from eucalyptus forest residues [33]. Nitrogen physisorption revealed the presence of a mesopores fraction that remained undetected by Hg porosimetry. Although these pores accounted for only a moderate fraction of the total pore volume, they significantly increased the specific surface area by raising it more than 2.5 times, from 5.8 m^2/g to 14.5 m^2/g. Given that the micropore volume is negligible (0.006 cm^3/g), the measured surface area can be primarily attributed to the mesoporous structure. The specific surface area of the wood ash exceeded the values reported for several comparable materials, including uncalcined *Acacia nilotica* wood ash (9.38 m^2/g) [12], calcined waste wood ash (1.10 m^2/g) [20, 36], and walnut shell ash (8.8 m^2/g) [24].

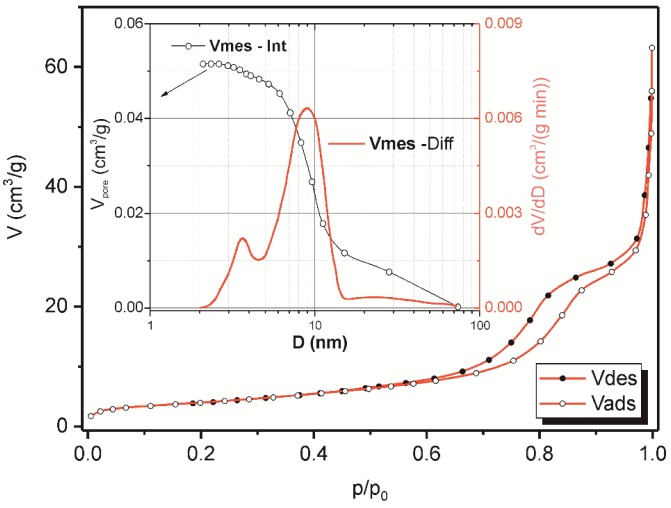

Figure 4. The nitrogen isotherm of wood ash; insert - integral and differential mesopore size distribution

At high relative pressures, the plateau transitions into a steep increase, accounting for nearly half of the total adsorbed nitrogen volume. This behavior is characteristic of Type II isotherms, typically associated with macroporous or non-porous materials. Consequently, the N_2 isotherm of wood ash is best described as a hybrid of Type IV and Type II forms. The complexity of the pore network is further evidenced by the shape of the hysteresis loop and the PSD curve. The hysteresis loop most closely resembles Type H5 according to the IUPAC nomenclature [35], which is characteristic of systems containing both open and partially blocked mesopores, typical of ink-bottle pore geometries [37]. In addition to the dominant maximum near 9 nm, a smaller peak at approximately 3.8 nm is observed in the PSD curve. This feature arises from cavitation, also known as the tensile strength effect, and confirms the existence of pores or pore necks with diameters smaller than the critical limit for nitrogen at 77 K [38].

SEM micrographs of wood ash (Figure 5) showed irregularly shaped particles and a porous surface, which is typical of wood ash obtained by combustion [39,40]. At higher magnification, the plate-like particles (agglomerates) can be observed, stacked in an overlapping manner (Figure 5b).

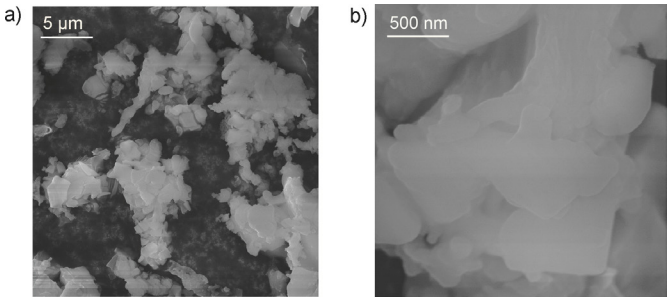

Figure 5. SEM micrographs of wood ash at magnification (a) 10000 and (b) 100000

The base strength of wood ash was in the range of $9.3 < H_- < 10$, while the total basicity was 0.012 mmol/g. In comparison, higher total basicity values have been reported in the literature for calcined waste wood ash (0.176-0.209 mmol/g) [20,36] and calcined *Acacia nilotica* wood ash (1.6-2.6 mmol/g) [12].

Sunflower oil methanolysis catalyzed by wood ash

The changes in FAME content during methanolysis of sunflower oil over wood ash with reaction time are presented in Figure 6. Conversion of TAG into FAME occurred rapidly within the first 10 min, indicating the absence of significant TAG mass transfer limitations. This behavior is consistent with reactions catalyzed by ash-based catalysts, as reported previously [9,24,41]. Increasing the catalyst loading from 5 wt.% to 15 wt.% significantly accelerated FAME formation, thereby enhancing the reaction kinetics. This effect can be attributed to the increased number of available active sites at higher catalyst loading [24,32]. However, at longer

reaction time (50-60 min), the FAME content converged to similar values, regardless of catalyst loading, suggesting that the reaction became equilibrium-controlled rather than kinetically controlled [31]. This observation indicated that although higher catalyst loading enhanced the reaction kinetics, it did not increase the conversion of TAG, implying the existence of an optimal catalyst loading beyond which further increases have a negligible effect on FAME content. Based on the obtained results, the optimal catalyst loading within the investigated range was the highest loading (15 wt.%), achieving a FAME content of 95.6±0.8% within 40 min, which further increased to 97.3±1.0% within 60 min. The relatively high catalyst loading may be attributed to the use of uncalcined ash and its composition, whereas other studies reported lower catalyst loadings for achieving comparable FAME contents using calcined ash-based catalysts [42]. For example, Sharma et al. [12] reported that increasing the loading of calcined wood ash from 1 to 3 wt.% resulted in an increase in FAME content to 97.7% after 180 min. Notably, Sharma et al. [12] found that specific surface and particle size were not correlated to catalytic activity, while Miladinović et al. [41] emphasized the relation of catalytic performance and catalyst composition. Previous studies on oil transesterification identified the catalyst loading as the most influential parameter affecting FAME content and yield [43]. Taslim et al. [13] found that biodiesel yield increased with increasing the catalyst loading of CaO-containing ash from 1 wt.% to 3 wt.%, while a further increase to 4 wt.% caused its decrease, indicating that the optimal catalyst loading exceeded. Maneerung et al. [31] reported that increasing calcined woody ash loading from 1 wt.% to 5 wt.% increased the FAME content in palm oil methanolysis, with no further improvement at higher catalyst loadings.

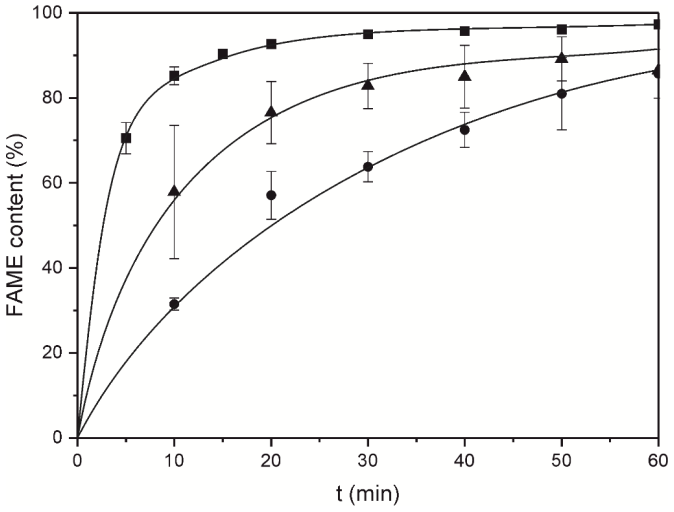

Figure 6. The effect of catalyst loading (● - 5 wt.%, ▲ - 10 wt.%, ■ - 15 wt.%) on the FAME content at methanol-to-oil molar ratio of 9:1 and temperature of 60 °C

From a stoichiometric perspective, an excess methanol-to-oil molar ratio is required to shift the reaction equilibrium toward FAME formation [44]. The influence of the methanol-to-oil molar ratio on FAME content and reaction kinetics, particularly its ability to shift the reaction equilibrium at shorter reaction times using a catalyst loading of 15 wt.%, was evaluated, and the results are presented in Figure 7. Increasing the methanol-to-oil molar ratio from 9:1 to 15:1 slightly increased FAME content and reduced the reaction time required to reach a FAME content >95%, from 40 min to 20 min. However, at the highest methanol-to-oil molar ratio of 15:1, a decrease in FAME content was observed at the initial stage of the reaction. This effect is attributed to the higher methanol amount, which can initially hinder effective mixing due to the increased reaction mixture volume. Although a higher methanol-to-oil molar ratio favored the reaction equilibrium, the associated methanol recovery and separation costs increased the overall production costs [45,46], and thus, this factor should be considered when determining the optimal molar ratio. The positive effect of the methanol-to-oil molar ratio on the biodiesel yield in the reaction catalyzed by CaO-containing ash, was observed when it increased from 6:1 to 9:1, but the higher methanol-to-oil molar ratio (12:1) caused a decrease in yield [13]. The methanol-to-oil molar ratio of 9:1 was found to be the optimal one. On the other hand, Sitepu et al. [47] investigated the influence of a broader range of methanol-to-oil molar ratios (9:1-21:1) on the FAME content in the transesterification of palm oil catalyzed by K-containing palm bunch ash. It was found that maximum conversion (92.6±0.6%) was achieved at a methanol-to-oil molar ratio of 15:1 and a constant reaction time (30 min), whereas a further increase in molar ratio led to a decrease in conversion due to glycerol solubility in excess methanol, causing the reversible reaction.

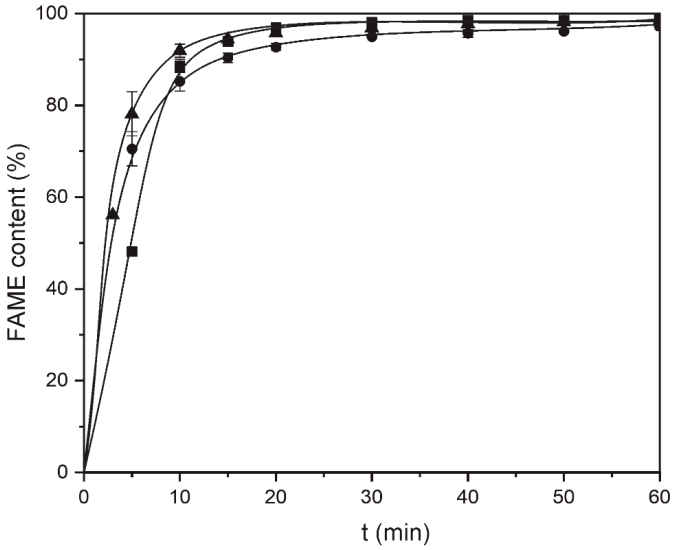

Figure 7. The effect of methanol-to-oil molar ratio (● - 9:1, ▲ - 12:1, ■ - 15:1) on the FAME content at catalyst loading of 15 wt.% and reaction temperature 60 °C

Catalyst reusability

The potential for reusing wood ash as a catalyst

was examined by testing its performance in consecutive reaction cycles, using 15 wt.% catalyst loading, a methanol-to-oil molar ratio of 9:1, and a reaction temperature of 60 °C. After reaction completion, the catalyst was separated from the reaction mixture by vacuum filtration and subjected to a second reaction cycle without further treatment, at a methanol-to-oil molar ratio 9:1 and a reaction temperature of 60 °C. No catalytic activity was observed for the untreated spent catalyst, indicating its deactivation. This could be attributed to contamination of the catalyst surface by reaction products, which leads to the blockage of active sites and consequent catalyst deactivation [41]. Previous studies on ash-based catalysts showed that catalyst regeneration is required to recover their catalytic activity. The most commonly used methods for recovering catalytic activity were washing and drying [36,48,49] or recalcination [24,41].

Economic aspect

Cost estimation is important for evaluating the feasibility of biodiesel production processes, especially when alternative catalysts or feedstocks are proposed. To date, no economic assessment has been reported for sunflower oil methanolysis catalyzed by wood ash. The present preliminary cost analysis included only operating costs and did not account for capital costs. The starting point for the preliminary analysis was methanolysis performed at the following reaction conditions: catalyst loading of 15 wt.%, a methanol-to-oil molar ratio of 9:1, reaction time of 40 min, and reaction temperature of 60 °C. The major contribution to the total cost was associated with oil feedstock (sunflower oil), accounting for approximately 80% of the total cost. Methanol contributed 11%, while electricity consumption per one cycle accounted for only 0.18% (Table 2). The estimated biodiesel production cost was 1.65 EUR/kg (or 1.42 EUR/L) of produced biodiesel. Increasing the methanol-to-oil molar ratio to 12:1 reduced the reaction time from 40 min to 20 min, which affected the energy consumption, however, the estimated cost increased to 1.72 EUR/kg (1.48 EUR/L), representing a 4.24% increase. This increase was primarily associated with the higher methanol amount. The estimated production cost for biodiesel in this study was higher than that typically reported for heterogeneously catalyzed processes, at approximately 1.2 EUR/L [50]. This difference highlights the current economic limitation of the proposed process, which is largely driven by the high cost of refined sunflower oil. Nevertheless, the process demonstrates considerable potential for future cost reduction. The implementation of methanol recovery may increase the production costs by approximately 2%, depending on the applied recovery strategy. However, the subsequent recycling of methanol, together with the utilization of other recovered streams such as glycerol, has been reported to reduce overall production costs by 36% [51]. Furthermore, the catalyst reuse can significantly contribute to cost reduction. For instance, reuse over five cycles of a CaO-rich catalyst derived from *Psidium guajava* L. leaves can reduce the production cost by 70-80% [52]. Therefore, in combination with optimized reaction conditions for achieving maximum FAME content, future studies should focus on evaluating catalyst stability and reusability alongside the use of alternative low-cost, non-edible oil feedstocks, thereby improving the overall economic viability of the proposed biodiesel production process.

Table 2. Preliminary cost analysis for biodiesel production from sunflower oil via methanolysis catalyzed by wood ash

Material/Process	Unit cost (EUR)	Quantity	Cost (EUR)
Sunflower oil	1.26 /kg	100 kg	126
Methanol	0.53 /kg	33 kg	17.5
Wood ash	0 /kg	15 kg	0
Electricity for the process	0.25 /kWh	1 kWhx0.67 h + 1 kWhx0.5 h	0.29
Net cost			143.79
Overhead (10% of net cost, includes labor, additional cost of washing, and chemicals)			14.38
Total cost		95.6 kg (111 L)	158.17
Cost per kg of biodiesel			1.65

Conclusion

Waste wood ash, generated as a by-product of solid-fuel combustion, was investigated as a heterogeneous catalyst for the transesterification of sunflower oil using methanol. Chemical and phase analyses confirmed that the catalyst was rich in Ca (43 wt.%) and K (18 wt.%), with dominant Ca- and K-containing crystalline phases. Morphological and textural characterization revealed a predominantly macroporous structure, characterized by a specific surface area of 14.5 m^2/g, porosity of 63%, and a total basicity of 0.012 mmol/g. Under mild reaction conditions, wood ash exhibited effective catalytic performance in sunflower oil methanolysis, enabling the rapid conversion of TAG into FAME, without observable TAG mass transfer limitations. The catalyst loading had a positive effect on the FAME content, with an optimal loading of 15 wt.% yielding a FAME content of 95.6% within 40 min. Furthermore, increasing the methanol-to-oil molar ratio reduced the reaction time required to achieve FAME contents above 95% to 20 min. Despite its high catalytic activity, the performance of wood ash was limited to a single reaction cycle, indicating the need for effective regeneration to restore and maintain catalyst activity. Overall, waste wood ash demonstrates strong potential as a sustainable and low-cost heterogeneous catalyst for biodiesel production, offering both economic and environmental benefits through the valorization of abundant waste material. Future studies should focus on catalyst regeneration, optimization of reaction parameters, and techno-economic assessment to evaluate the feasibility of this process for large-scale biodiesel production.

Nomenclature

Abbreviations

TAG	Triacylglycerols
FAME	Fatty acid methyl esters
HPLC	High-pressure liquid chromatography
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
TGA-DSC	Thermogravimetric analysis and differential scanning calorimetry
XRD	X-ray diffraction
SEM	Scanning electron microscopy

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Izvod

KATALITIČKA AKTIVNOST OTPADNOG DRVNOG PEPELA U METANOLIZI SUNCOKRETOVOG ULJA

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Otpadni pepeo nastao sagorevanjem biomase, kao što je pepeo drveta, predstavlja perspektivnu i jeftinu sirovinu za industriju biodizela jer se pretežno sastoji od oksida alkalnih i zemnoalkalnih metala. U ovom radu istraživana je proizvodnja biodizela iz suncokretovog ulja putem metanolize katalizovane otpadnim pepelom drveta. Katalizator je detaljno okarakterisan u pogledu termičkog ponašanja, hemijskog i faznog sastava, teksturalnih svojstava, morfologije i bazne jačine. Hemijska analiza je pokazala da su Ca (43 wt.%) i K (18 wt.%) dominantni elementi, što je u saglasnosti sa XRD analizom, kojom su njihovi oksidi identifikovani kao glavne kristalne faze. Katalitička aktivnost otpadnog pepela drveta ispitivana je u šaržnim uslovima na temperaturi 60 °C i pri količini katalizatora u opsegu 5–15 wt.%, u odnosu na masu ulja, i molarnom odnosu metanol-ulje od 9:1 do 15:1. Uočena je brza konverzija triacilglicerola (TAG) u metilestre masnih kiselina (MEMK), što ukazuje na zanemarljiva ograničenja prenosa mase u reakcionom sistemu. Povećanje količine katalizatora pozitivno utiče na brzinu nastajanja MEMK, pri čemu je utvrđeno da optimalna količina katalizatora u ispitivanom opsegu iznosi 15 wt.%. Iako je molski odnos metanol-ulje imao slab uticaj na konačan sadržaj MEMK, pri većim vrednostima ovog odnosa vreme potrebno za postizanje sadržaja MEMK >95% smanjuje se sa 40 na 20 min, pri optimalnoj količini katalizatora. Uprkos relativno visokoj ceni sirovine ukazanoj preliminarnom analizom troškova, dobijeni rezultati pokazuju da je otpadni pepeo drveta efikasan katalizator za proizvodnju biodizela, iako je njegova katalitička aktivnost ograničena na jedan reakcioni ciklus.

Ključne reči: biodizel, heterogena kataliza, pepeo drveta, varolizacija otpada

CRediT authorship contribution statement:
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