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Original Research Article

Functionalized Sepiolite Nanocatalyst under Radiative Heating for Cyclic Biodiesel Production

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ABSTRACT

Biodiesel production is energy-consuming and requires an appropriate catalyst to boost the reaction. In the present study, waste edible oil was used as the feedstock, an infrared lamp was utilized as the heat source, and a solid acid catalyst based on sepiolite (Sep) clay was applied. The sepiolite catalyst was modified with chlorosulfonic acid and exhibited a nanoscale particle size distribution. The effects of infrared irradiation on the reaction time and quality of the oil-methanol-catalyst system were investigated and compared with conventional electric heating. Material properties were characterized by XRD (X-ray diffraction) and FE-SEM (field-emission scanning electron microscopy), and the biodiesel yield and quality were evaluated by GC-MS (gas chromatography-mass spectrometry) analysis. The experimental results demonstrated that the sepiolite nanocatalyst achieved a high biodiesel yield of 96.5% under infrared irradiation, about 4% higher than that of the conventional heating under the same conditions. Meanwhile, radiation heating reduced energy consumption per liter by 68% compared to electric heating. The biodiesel production cost on a laboratory scale was estimated at 1.26 to 1.65 $/lit for the infrared irradiation and 1.68 to 2.62 $/lit for the electric heating method. The separation and recovery of the catalyst from the transesterification reaction products were also studied and found to be easier, faster, and simpler than those of homogeneous catalysts. The catalyst was successfully reused for three successive cycles, with less than a 2% reduction in the yield per cycle, and still showed a biodiesel yield of above 90%.

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1. INTRODUCTION

The growing demand for fuel due to population growth, along with environmental concerns associated with fossil fuel use, has driven the shift toward green energy. Biodiesel is a promising alternative to fossil fuels due to its biodegradability and non-toxicity (Garmroodi et al., 2016).

Biodiesel can be synthesized using various methods, with transesterification being the most widely used. Transesterification is a well-established reaction that produces biodiesel and glycerol from oil or fat and alcohols such as methanol. This process occurs in three consecutive steps: (1) conversion of triglycerides to diglycerides, (2) conversion of diglycerides to monoglycerides, and (3) conversion of monoglycerides to glycerol (Al-Ani et al., 2018).

The transesterification process is kinetically limited and requires a catalyst to accelerate the reaction rate and achieve high conversion. The catalysts used in this process can be classified as homogeneous or

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heterogeneous catalysts (Aghababaeian et al., 2023). They can also be categorized as acid or base catalysts. Base catalysts exhibit higher reaction rates at lower temperatures and offer greater product selectivity (Kasirajan, 2021). However, alkaline catalysts are incompatible with high free fatty acid content in the feedstock, limiting their use to materials with less than 0.5 wt% free fatty acid. Otherwise, saponification occurs as an undesired side reaction. Acid catalysts are required when the free fatty acid content is higher (Jacobson et al., 2008).

Homogeneous catalysis occurs when the catalysts and reactants share the same phase, typically liquid or gaseous (Mohadesi et al., 2019). In contrast, heterogeneous catalysis involves solid catalysts, creating phase boundaries between the catalyst and the reactant mixture (Narasimhan et al., 2021). Biodiesel production is commonly catalyzed by homogeneous catalysts due to their low cost and high efficiency. However, these catalysts have drawbacks, such as product contamination and a high dependency on edible vegetable oils. Heterogeneous catalysts can overcome these issues, as they do not dissolve in the product, facilitating separation and improving quality. Additionally, heterogeneous catalysts can be recycled and reused for multiple cycles with proper regeneration (Esther Olubunmi et al., 2022).

Various categories of heterogeneous catalysts are used in biodiesel production, including derivatives of alkali metal oxides (Arzamendi et al., 2007), alkaline earth metal oxides (Yoo et al., 2010), metal oxides, ion exchange resins, sulfated oxides (Jumina et al., 2021), carbon-based materials, and enzymes (Ashjari et al., 2020). Sepiolite, which has catalytic sites similar to those of MgO (Murguía-Ortiz et al., 2021), ZnO (Dasta et al., 2022), or Al_2O_3 (Kesserwan et al., 2020), is a promising candidate for catalysis.

Several studies have explored the use of sepiolite, a readily available and inexpensive material, as a catalyst for biodiesel production. Composite catalysts based on clay minerals are particularly promising due to their environmental friendliness, biocompatibility, and non-toxicity (Dassanayake et al., 2023 and Monsef & Salavati-Niasari, 2023). For instance, in one study, pig pancreatic lipase was immobilized on sepiolite as an enzymatic catalyst for biodiesel synthesis, demonstrating superior performance compared to conventional base catalysts while also being recyclable (Caballero et al., 2009). Another study reported the use of natural porous sepiolite as a hydrated magnesium silicate catalyst for biodiesel synthesis via transesterification, achieving a biodiesel yield of 96.5% (Degirmenbasi et al., 2014). Additionally, the catalytic performance of a NaOH/Sep nanocomposite base catalyst was evaluated for biodiesel synthesis from canola oil, resulting in a biodiesel conversion rate of 93.8% (Aslan et al., 2019). Recently, Aghababaian et al. (Aghababaeian et al., 2023) proposed a nano-sulfonated sepiolite (Sep-SO_3H) as a heterogeneous catalyst for an efficient transesterification process. The catalytic role of this nanocatalyst was introduced, demonstrating the superior performance of the Sep-SO_3H catalyst.

The transesterification process is an endothermic reaction. Various heating techniques have been employed to facilitate this reaction, including conventional heating, hybrid heating (Karan & Chakraborty, 2023), infrared heating, microwave (Arpia et al., 2021), radio frequency, and ultrasound (Elgharbawy & Ali, 2022). In conventional heating, the reactor is heated via a heated surface (such as an electrical heating element or a heat exchanger), where heat is transferred to the reactant mixture through convection within the fluid. In this convective heat transfer method, heat must propagate from a heated surface through the molecular movement of the fluid mixture (Fattahi et al., 2022). In contrast, radiative heating does not require a medium for energy transfer. Instead, it allows heat to be directly absorbed by the entire reactant mixture. This direct heating mechanism ensures uniform temperature distribution throughout the reaction medium, reducing the heat gradient and exergy loss. Compared to conventional methods that rely on convection, radiative heating is significantly more energy-efficient due to its lower temperature gradient (Dehghan et al., 2020).

Chakraborty and Sahu (Chakraborty & Sahu, 2014) were the first to explore the use of infrared irradiation for the transesterification of waste mustard oil, reporting that infrared heating enabled fast and efficient biodiesel production. Their study demonstrated that infrared-assisted transesterification was energy-efficient for biodiesel synthesis from waste mustard oil. Kusumo et al. (Kusumo et al., 2017) compared ultrasound and infrared heating techniques for biodiesel production, achieving biodiesel yields of 99.41% and 98.55%, respectively, within one hour using KOH as a catalyst (Kusumo et al., 2017). Most recently, Aghababaeian et al. (Aghababaeian et al., 2024) showed that utilizing radiative heating with solid catalysts resulted in lower specific energy consumption and production costs, making it a promising approach for large-scale biodiesel production.

The present study aimed to compare the transesterification of waste edible oil using a sepiolite-based heterogeneous acid catalyst under two different heating methods: infrared irradiation and conventional heating. Natural sepiolite was used to stabilize the sulfonic acid catalyst for biodiesel production.

2. Materials and Methods

The materials used in the experiment are shown in Table 1.

TABLE 1. Materials used in the present experiments

Name	Formula or specifications	Purity %	Source
Sunflower oil	-	-	Waste
Methanol	CH_3OH	99/5	Commercial grade
Sepiolite	-	-	Iranian mines
Nitric acid	HNO_3	65	Merck
Dichloromethane	CH_2Cl_2	-	Merck
Chlorosulfonic acid	$ClSO_3H$	85	Merck
Normal hexane	C_6H_{14}	95	Merck
Magnesium sulfate	$MgSO_4$	70	Merck
Isopropyl alcohol	C_3H_8O	-	Merck
Infrared lamp	Near-infrared lamp, 150W and 230V	-	O.S.R.A.M.

To prepare the required catalyst, sepiolite was first treated with nitric acid and then reacted with chlorosulfonic acid in dichloromethane for 30 minutes. It was then washed and dried. The oil was passed through a paper filter to remove solid impurities. Transesterification of the oil to produce biodiesel was carried out using two heating methods: infrared heating and conventional electric heater heating. The conventional method employed a 250 mL flask equipped with an electric heater, stirrer, and condenser. In contrast, the radiative method used a 5 L insulated beaker with a lid, equipped with a near-infrared lamp, condenser, magnetic stirrer, dimmer, and thermostat. In both reactors, 100 grams of filtered and preheated oil were added and heated to the reaction temperature. The methanol-catalyst mixture was then added at a predetermined ratio, and the reaction was maintained for a specified duration at 64 °C with stirring at 800 rpm.

After each reaction, the catalyst or residual glycerol was separated using a separator funnel and washed with distilled water. The phases were allowed to separate, and the upper layer (i.e., the desired methyl ester) was collected and centrifuged for 20 minutes at 4000 rpm. Anhydrous magnesium sulfate was added as a drying agent to the methyl ester and centrifuged again. Finally, the produced biodiesel was analyzed by gas chromatography-mass spectrometry (GC-MS) to determine its composition and concentration. The biodiesel sample was dissolved in normal hexane for injection into the GC-MS device.

The possibility of reusing the sepiolite nanocatalyst was tested by washing it several times with isopropyl alcohol. The recovered catalyst was used for three cycles under the same optimal transesterification reaction conditions.

3. Results and Discussion

3.1. Characterization

The analyses performed on the sepiolite nanocatalyst and the equipment used during the experiments are summarized in Table 2.

Table 2. Characterization methods used in the present study

Analysis	Device model	Specification / Result
XRD	X'pert M.P.D. Philips PW371 with Cu Ka radiation (λ =1.5406 Å).	The functionalized sepiolite has an amorphous SiO_2 (Figure 1).
FESEM	MIRA3 TESCAN	After functionalization, sepiolite lost its fibrous structure and found a magnesium-silicate state with a particle size of below 100 nm (Figure 2).
GC-MS	GC-MS-Agilent-6890N	Yield of biodiesel.

Figure 1 shows the XRD patterns of the nanocatalyst Sep-SO3H. In the XRD pattern, the peaks related to silica and dolomite are identified as amorphous silica, while the peaks at 2θ = 28°, 31°, and 48.6° correspond to dolomite ($CaMg(CO_3)_2$).

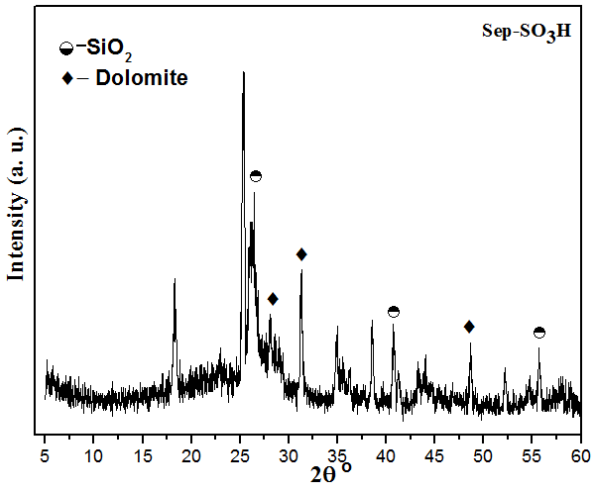
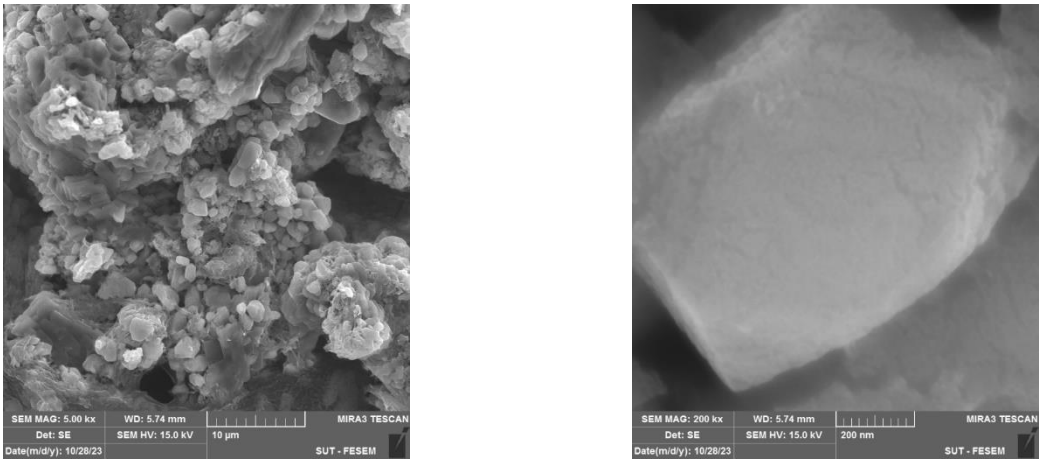


Figure 1. X-ray diffraction pattern of the functionalized nanocatalyst (Sep-SO3H).

The SEM images of the nanocatalyst Sep-SO_3H are shown in Figure 2. The images indicate that the chlorosulfonic acid reaction with the sepiolite produced

an amorphous silicate containing dolomite. The EDX pattern (Figure 3) of the sulfonic acid-functionalized nanocatalyst Sep-SO_3H reveals the presence of Si, O, Ca, Mg, and S in the nanocatalyst. Additionally, the elemental mapping further confirmed a homogeneous distribution of the elements in Sep-SO_3H.



(a) (b)

Figure 2. The FE-SEM images of functionalized Sep-SO3H catalyst with the magnification of (a) 5kx and (b) 200kx.

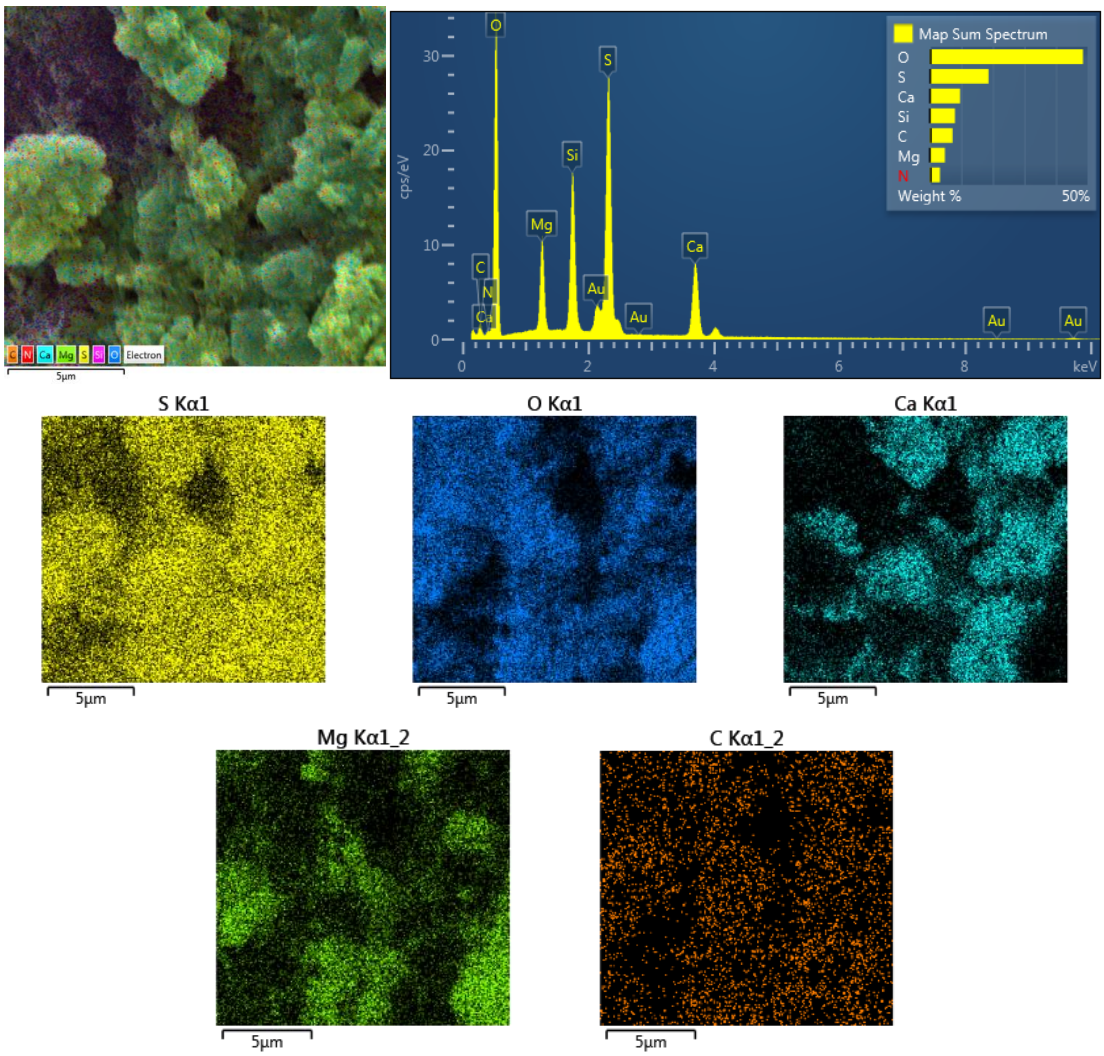


Figure 3. EDX spectrum and X-ray atomic map of the functionalized Sep-SO3H nanocatalyst.

3.2. Biodiesel yield

It is worth mentioning that the optimal values of the main influencing parameters, including temperature, methanol-to-oil molar ratio, catalyst type, purity, loading, and reaction time, vary depending on the specific characteristics of the feedstock and process conditions to maximize biodiesel yield while minimizing costs and environmental impacts. Careful and extended experiments are required to optimize biodiesel yield when using an acid catalyst. Catalyst concentration should be optimized to achieve maximum yield without causing side reactions or excessive soap formation (Sirsam et al., 2016). Excess methanol can drive the reaction forward, but too much can lead to side reactions and waste. Transesterification reactions are exothermic, meaning they release heat. The reaction temperature affects the rate of reaction and, consequently, the yield (Sani et al., 2023). Optimal temperatures usually range from 50°C to 65°C. Higher temperatures can accelerate the reaction but may also lead to the degradation of biodiesel. Longer reaction times can increase yield up to a certain point, beyond which it may lead to soap formation and decreased yield (Stanescu et al., 2023). Higher catalyst concentrations generally lead to higher yields, but there is an optimal concentration beyond which the yield may not increase further or may even decrease due to side reactions (Ting et al., 2008).

As mentioned above, although the stoichiometric ratio for this reaction is 3:1, higher ratios are usually required to shift the equilibrium toward biodiesel formation. The optimal conditions for the transesterification of waste edible oil with the sepiolite nanocatalyst were reported as a 12:1 molar ratio and 2 wt.% catalyst loading. The reaction time of the biodiesel production process is analyzed in Figure 4 for the conventional and infrared heating methods under the conditions mentioned in Section 2. Figure 4 shows that infrared heating achieved a higher biodiesel yield (up to 2%) in a shorter reaction time (4 hr) than conventional heating. Results revealed that the time for the transesterification process under radiative heating is 4 hours. The reusability of the sepiolite nanocatalyst was also evaluated for three cycles, and the biodiesel yield was 90.4% in the last cycle.

The quality of the biodiesel product and the biodiesel yield were evaluated by gas chromatography analyses (GC-MS), as shown in Figure 5. The chromatogram exhibited four major peaks corresponding to the methyl esters of hexadecanoic acid ($C_{17}H_{34}O_2$), 9,12-octadecadienoic acid ($C_{19}H_{34}O_2$), 9-octadecenoic acid ($C_{18}H_{34}O_2$), and octadecanoic acid ($C_{18}H_{36}O_2$). The biodiesel yield was calculated as the total percentage of these four peaks. The presence of other minor peaks indicated some impurities in the product.

To compare with available studies, Table 3 shows the biodiesel yield obtained using sepiolite-based catalysts. The first column lists the materials used to enhance the sepiolite catalytic performance. All these studies used fresh oil as the feed, while the present study used waste edible oil as the raw material. Considering this, the yield obtained by the prepared sepiolite nanocatalyst in the present study is comparable to the available results in the literature. Additionally, all the previous studies used fresh catalysts, whereas the present study reused the sepiolite after three successive cycles, achieving a final yield of over 90%.

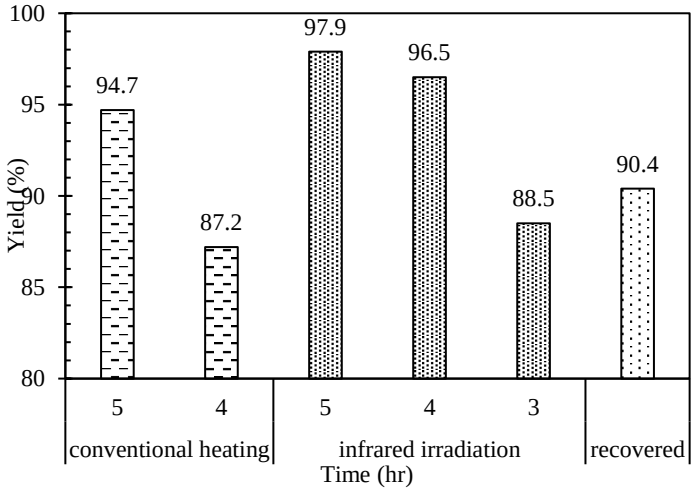


Figure 4. Investigating the effect of the reaction time on the biodiesel yield of the prepared sepiolite nanocatalyst.

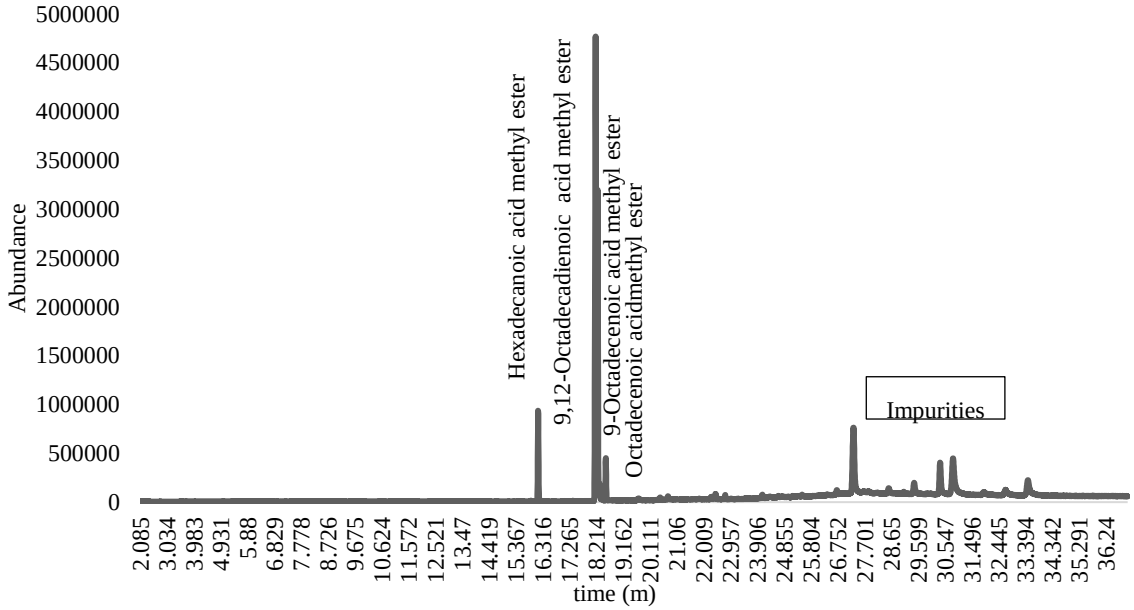


Figure 5. An example chromatography of the tests.

TABLE 3. Studies conducted on Sepiolite-based heterogeneous catalysts

Catalyst type/ Sepiolite	Feed	Oil to alcohol (molar) ratio Catalyst wt%	Reaction temperature (°C) Reaction time (min)	Heating method	Biodiesel yield (%)	Ref.
K_2CO_3	Forage turnip oil	1:12 2 wt.%	70 °C 240 min	Electric heater	99	(Dussán et al., 2019)
NaOH	Canola oil	1:9 6 wt.%	60 °C 180 min	Electric heater	80.93	(Aslan et al., 2019)
K_2CO_3	Canola oil	1:6 3 wt.%	65 °C 480 min	Electric heater	98.5	(Degirmenbasi et al., 2014)

3.3. Energy and cost of biodiesel production

The specific energy and cost required to produce 1 L of biodiesel from waste edible oil using the sepiolite catalyst were compared for infrared and electric heating methods. Figure 6 shows that infrared heating consumed less energy (three times lower than electric heating) and achieved a higher biodiesel yield (up to 2%, as seen in Figure 4) in a shorter reaction time (at least 1 hour) compared to electric heating. Therefore, considering energy consumption, radiative heating performs better than conventional heating. The specific cost (i.e., the production cost of one liter of biodiesel, $/L) in the present laboratory-scale study, shown in Figure 7, includes raw materials, catalyst, and energy consumption. The electricity prices were taken as 0.05 and 0.2 US$/kWh to cover both low and mid-range energy prices (Eurostat). The results indicate that infrared heating reduces the production cost by 37% compared to conventional electric heating at an energy price of 0.2 $/kWh. By reducing the energy price to 0.05 $/kWh, the share of energy in the total cost decreases, and thus the cost reduction also decreases. In this case, the specific cost of biodiesel produced with radiative heating is still 25% lower than that of conventional heating.

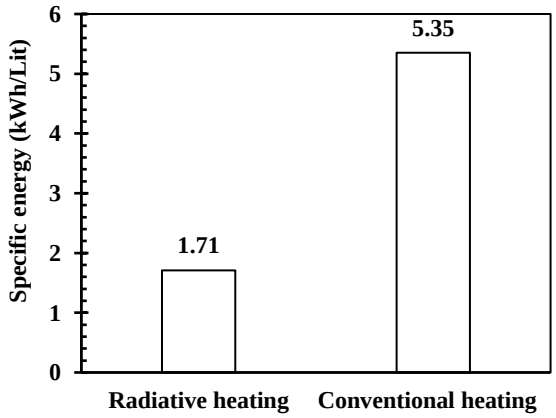


Figure 6. Comparison of the reaction energy consumption with radiation heating method and electric heater to produce 1 liter of biodiesel.

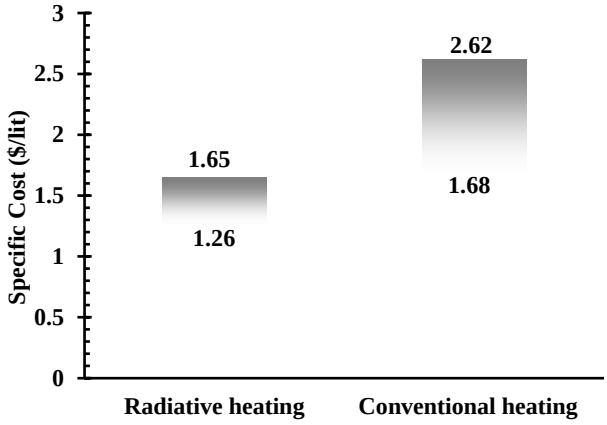


Figure 7. Specific biodiesel production cost for conventional and infrared heating methods.

4. CONCLUSIONS

A cost-effective solid acid catalyst was used to efficiently produce biodiesel from waste edible oil, with performance enhanced by infrared heating. The sepiolite nanocatalyst was prepared by functionalizing sepiolite with chlorosulfonic acid. The results showed that the infrared heating method increased transesterification efficiency and reaction speed, while also reducing reaction time compared to the electric heating method. The optimal conditions for biodiesel production from waste edible oil using the sepiolite catalyst and infrared heating were determined to be a 12:1 molar ratio of methanol to oil, 2% (by weight) catalyst loading, a reaction time of 4 hours, and a reaction temperature of 64°C. Under these conditions, the biodiesel yield was 96.5%. The cost of producing 1 liter of biodiesel using infrared heating was approximately 25% to 37% lower than that of electric heating. The reusability of the sepiolite catalyst was also evaluated over three consecutive cycles, with the biodiesel yield decreasing by an average of 1-2% per cycle, reaching 90.4% in the fourth cycle.

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