Indian Journal of Chemical Technology
Vol. 32, July 2025, pp. 497-503
DOI: 10.56042/ijct.v32i4.10402

Utilizing Peganum harmala plant as a catalyst for producing biodiesel from waste cooking oil: A practical method for recycling used oil into biodiesel

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Received 13 April 2024; accepted 30 June 2025

The present study proposes use of waste cooking oil (WCO) as a useful resource in the manufacturing of biodiesel as well as reduction of production costs for the additive. The goal of this research is to optimize the process parameters for biodiesel production within the permissible limit values given in the literature. This research focuses on maximizing output yield by using composite heterogeneous catalysts, namely the Pegnum harmala plant. The catalysts are calcined at 800°C for 4 h to boost catalytic activity and surface area. An experiment was designed using the transesterification approach. The highest production of fatty acid ethyl esters is achieved via experimentation at 85%. This is accomplished by using calcined harmala plant with an ethanol to waste cooking oil molar ratio of 10:1, a catalyst loading of 3%, and operating at a temperature of 80°C for duration of 3 h. The fuel characteristics of fatty acid ethyl ester are consistent with ASTM, indicating that it is a viable alternative fuel source. It is admirable to use biodiesel obtained from waste and untapped resources to develop and implement a more sustainable and environmentally sensitive energy strategy. Adoption and integration of green energy methods has the potential to provide beneficial environmental consequences, supporting improved social and economic growth for the biodiesel industry as a whole.

Keywords: Biodiesel, Pegnum harmala, Transesterification, Waste cooking oil

Introduction

Recently, there has been a significant global concern regarding the excessive utilization of natural energy resources, the continuous escalation of environmental degradation, and the subsequent phenomenon of global warming. The situation has become even more dire as a result of industrialization and improvements in the level of life in society[1-3]. The impending depletion of fossil fuel reserves has prompted researchers to reevaluate the feasibility of using these resources and instead focus on developing alternative energy sources and cutting-edge technological approaches for lowering energy consumption and waste production. Numerous studies have shown that biofuels more specifically, biodiesels may be the most promising and feature-rich green fuel option for alternative energy sources[4-7].

Biodiesel is classified as "green energy" or "green fuel" due to its composition, which primarily comprises lower alkyl fatty acids (chain length C_{14}–C_{22}) and esters of short-chain alcohols (methanol or ethanol)[8]. Biodiesel is predominantly manufactured using oils derived from food waste, crop oils, wild plant oils, microalgae aquatic plant oils, and animal lipids[9]. Nevertheless, a significant impediment to the manufacturing of biodiesel lies in the financial burden associated with acquiring raw materials. The elevated cost of raw materials has a direct impact on the overall cost of biodiesel, hence impeding its widespread manufacturing[10]. However, it is crucial to consider the equilibrium between biodiesel feedstock and the ongoing food crisis. One viable and promising alternative is to generate biodiesel using non-edible plant seed oils as a feedstock. A non-edible feed plant that produced seeds with a high oil yield, a brief growth cycle, and a high oil content[11-13] was preferred in this context.

Peganum harmala is a perennial herbaceous plant classified under the family Zygophyllaceae. The whole plant displayed hypertrophy, characterized by an abnormal increase in size. Additionally, the elongated roots of the plant emitted a distinct odor. Peganum harmala, also known as Plantagolanceolata, is often found in several natural habitats such as desert regions, dry grasslands, the edges of oases, sandy areas with mild salinization, loamy low hillside regions, and valley dunes. The distribution of the Peganum harmala plant encompasses several

locations, including Mongolia, Central Asia, West Asia, Iran, northwest India, the Mediterranean region, and North Africa. It is important to acknowledge that Peganum harmala exhibits toxicity, rendering it unsuitable for consumption. Consequently, this characteristic increases the potential for PHL to be used as a feedstock for biodiesel production[14].

This work aimed to synthesize biodiesel from waste cooking oils by the use of a catalyst derived from the harmala plant as this study is the first study to our knowledge used this catalyst for production of biodiesel. Furthermore, an examination was conducted on the fuel characteristics of biodiesel production, revealing that waste cooking oils had significant potential as viable feedstock for the manufacture of biodiesel.

Experimental Section

Materials

The transesterification reaction is consistently influenced by the reaction parameters. In order to optimize the production of biodiesel, it is crucial to identify the optimal parameters for the transesterification process. This study examined four distinct factors related to transesterification: the molar ratio of waste cooking oil to ethanol ranging from 1:3 to 1:12, the concentration of catalyst ranging from 1-5 wt.% (with the catalyst mass determined based on the weight of waste cooking oil), the reaction temperature ranging from 60-80°C, and the reaction duration ranging from 1-4 h.

Pre-treatment and characteristics of WCO

The oil obtained was kept under normal atmospheric conditions. After that, it was filtered through a 110 nm sieve to eliminate any significant food contaminants and residue. Furthermore, it was set to 110°C to remove any leftover water content. After the process of filtering and dehydration, many physicochemical parameters of waste cooking oil (WCO) were determined such as density, free fatty acid value, kinematic viscosity, and molecular weight. Table 1 displays the findings according to the physicochemical parameters. The fatty acid content was determined by gas chromatography and the results are shown in Table 2.

Preparation of catalyst and its characterization

Harmala plant, collected from desert in Empty Quarter in Saudi Arabia, was used to develop cost-effective and eco-friendly catalysts. After undergoing many rinses with hot water, the harmala plant was subjected to a drying process in sunlight for duration of 12 h. Subsequently, those were transferred to an oven that had been set to a temperature of 100°C, where they were left for a period of 2 h. The dried harmala plant was first pulverized into a fine powder using a mortar. Subsequently, the powder was subjected to calcination in a muffle furnace, with temperatures varying between 600 and 1000°C (depend on thermogravimetric analysis results). The heating process occurred at a rate of 15°C per minute, lasting a total of 3 h. Following calcination, the resulting material was stored in a hermetically sealed glass container. Fig. 1 shows the preparation of the catalyst. Several analytical techniques, including as X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) analysis, thermogravimetric analysis (TGA), and SEM-EDX were used in the investigation of catalysts obtained from harmala plant.

Transesterification reaction

The transesterification procedures were conducted using a round-bottomed glass flask reactor with a

Table 1 — Physicochemical traits of waste cooking oil

Characteristics	Measured value
Density (kg/m^3)	0.9
Free fatty acid %	0.8
Viscosity @40◦C	43
Molecular weight	875

Table 2 — Fatty acid composition of waste cooking oil

Fatty acid	Composition (%)
Methyl myristate (C14:0)	0.11
Palmitic acid (C16:0)	2.11
Oleic acid (C18:1)	3.32
Linoleic acid (C18:2)	58.32
Arachidic acid (C20:0)	0.48

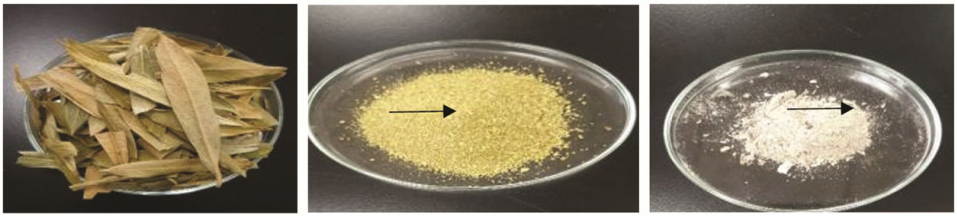

Fig. 1 — Preparation of the catalyst (a) Pegnum harmala after collecting and drying, (b) after grinding and (c) after calcination

volume of 100 cm^3, equipped with a reflux condenser and agitated magnetically, as seen in Fig. 2a. The catalyst was subjected to a temperature of 50°C for 40 min, while being agitated in an ethanol solution of a specific concentration. Subsequently, the reaction mixtures were heated within a temperature range of 60 to 90°C using a hot-plate. In a typical reaction, the catalyst was used at a concentration ranging from 1% to 5%. Additionally, the molar ratio of ethanol to WCO was employed as per the needed specifications. Following the designated reaction period, the mixture was then cooled to attain ambient temperature. Upon completion of the reaction, the solution was transferred into a separate funnel. Glycerol, and ethyl ester were separated into distinct layers. The product was allowed standing overnight to effectively separate. Different stages are clearly distinguished after an overnight stand, as seen in Fig. 2b. The biodiesel layer was then combined with 15 mL of distilled water and agitated on a hotplate for 15 min before being transferred to a separating funnel and allowed for 24 h to produce two clear layers. The bottom layer was removed, and the biodiesel layer was combined with 0.05 g of sodium sulfate and agitated for 10 min before being separated to determine its weight. Catalysts that have been retrieved are reused in the succeeding reaction. Fig. 1 depicts the biodiesel manufacturing processes from WCO used in the current investigation.

The studies were repeated in order to determine the biodiesel production. The biodiesel yield refers to the percentage of the mass ratio between the biodiesel generated and the total mass of the waste cooking oil used. The %yield was calculated using the following equation.

$$\text{Yield } \% = \frac{Weight\ of\ biodiesel\ produced}{Weight\ of\ sample\ oil\ used} \text{ x } 100 \quad (1)$$

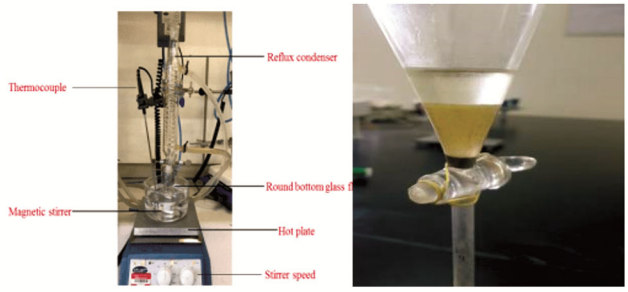

Fig. 2 — (a) Glass reactor for synthesis of biodiesel and (b) biodiesel separation after one-night stand biodiesel (the top layer) and glycerol

Results and Discussion

The WCO (Waste Cooking Oil) was used for the purpose of direct transesterification in order to investigate the impact of altering the catalyst concentration, the ethanol-to-oil molar ratio, and the reaction duration, while maintaining all other parameters at a constant level. The findings are further upon in the following sections.

Characterizations of the catalyst

Both the BET surface area and the pore volume of the calcined catalyst at 800°C (C800) were shown to be much higher than those of other catalysts (Table 3). Because of the catalyst's larger surface area and pore volume, it was able to display a higher level of catalytic activity during the process of transesterification of WCO, which was necessary for the production of biodiesel. As a result of this, the C800 catalyst was chosen for the purpose of maximizing the properties of the biodiesel.

Fig, 3 shows the XRD patterns of the calcined Pegnum harmala. When the calcination temperature

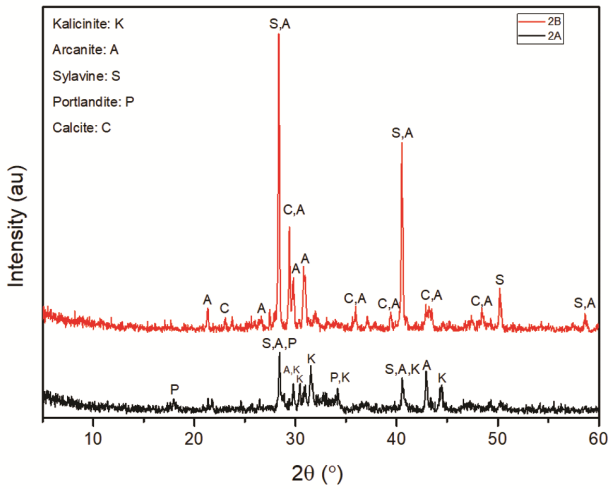

Fig. 3 — XRD results for synthesized catalysts from Pegnum harmala plant calcined at (a) 600 and (b) 800°C

Table 3 — BET analysis of Pegnumharmala plant catalyst at different calcination temperature

Calcination temperature (°C)	Surface area (m^2 /g)	Pore size (nm)	Pore volume (cm^3 /g)
uncalcined	57.8505	1.9327	0.055905
600	87.4621	4.1507	0.18151
800	132.957	1.5711	0.19445
1000	100.234	1.976	0.23445

was raised from 600 to 800℃, the peaks due to potassium carbonate and calcium hydroxide disappeared, while the peaks due to potassium sulfite and calcium carbonate became more significant and sharp.

The SEM examination was used to examine the morphological microstructure of the calcined Pegnum harmala, as seen in Fig. 4. The presence of surface heterogeneity may be inferred from the rough and uneven microstructure seen on the surface.

The composition of the sample surface was investigated using EDX as shown in Table 4. EDX confirmed the presence of Ca and P as the major identified elements of the calcined sample with compositions of 35.54% and 17.33%, respectively, which is responsible for providing active basic sites on the surface of the catalyst.

Transesterification catalytic activity

Effect of varying calcination temperatures on catalyst activity

It is critical to recognize that the principal aim of calcination is to eliminate secondary crystalline phases, thereby enabling the progression of the intended phase. As shown in Table 5, the effect of activation temperature on transesterification activity was examined for the selected feedstock over the temperature range of 600-1000℃. The application of calcination on the catalyst enables the elimination of secondary phases, resulting in increased crystallinity and particle compaction. The study's results revealed a clear association between increasing the calcination temperature of harmala plant material and the subsequent increase in biodiesel production. The catalyst that was calcined at 800℃ showed the highest catalytic activity compared to the other catalysts. After being calcined at 800℃, the catalysts (referred to as C800) showed significant catalytic activity, likely due to the optimal amount of active basic sites on the catalyst's surface. The magnitude of a catalyst's surface area has a significant impact on the accessibility of reactants to its active sites. As a result, the catalyst's activity and effectiveness in the transesterification process are directly influenced. Consequently, the C800 catalyst was selected in order to improve the characteristics of biodiesel. The catalyst shows considerably improved efficiency when the calcination temperature is increased to 800℃, as shown by the results from the larger surface area of this catalyst. Therefore, the catalyst stated before was selected for further study.

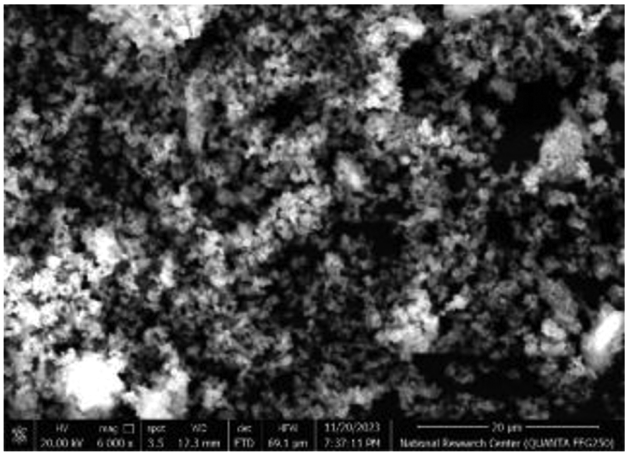

Fig. 4 — SEM analysis for calcined catalyst derived from Pegnum harmala plant

Effect of the concentration of the catalyst

The significance of the catalyst quantity in biodiesel synthesis reactions has been established. The occurrence of the reaction is shown to be quite unlikely in the absence of a catalyst. Nevertheless, in

Table 5 — Effect of varying calcination temperatures on the catalytic activity

Calcination temperature (℃)	Biodiesel yield (%)
Uncalcined	11
600	68
800	85
1000	78

Reaction conditions: catalyst loading 3 wt%, reaction time 3 h, reaction temperature 80℃, oil to ethanol molar ratio 1:10

Table 4 — EDX analysis for the synthesized catalyst

Element	Weight %	Atomic %	Net Int.	Error %
O K	44.31	64.67	65.24	12.03
MgK	0.63	0.6	5.09	45.37
AlK	0.21	0.18	2.23	67.8
SiK	0.23	0.19	2.98	64.69
P K	17.33	13.07	203.03	4.47
AgL	0.29	0.06	1.78	63.69
CaK	35.54	20.71	290.22	2.94
ZnK	1.46	0.52	2.79	62.12

the event that there is an excessive quantity of catalyst, the reactants are unable to adequately engage with the catalyst due to poor mixing within the reaction mixture, resulting in a drop in reaction efficiency. Insufficient use of catalysts results in suboptimal reaction efficiency. Hence, it is vital to conduct an investigation into the optimal quantity of catalyst. The investigation focused on examining the impact of catalyst concentration on the optimization process under certain conditions, including a ethanol-to-oil molar ratio of 10:1, a reaction temperature of 80°C, a stirring speed of 800 rpm, and a reaction period of 180 minutes (Fig. 5). The authors of the study hypothesized that a catalyst with many highly reactive basic sites and a large surface area would demonstrate considerable levels of activity[13]. In the context of this investigation, the concentration of the catalyst was varied at levels of 1% to 5% relative to the weight of the oil. The quantity of biodiesel production exhibited an upward trend with the addition of larger quantities of the catalyst. Notably, the highest yield of biodiesel was achieved when 3% of Pegnum harmala plant catalyst was introduced, resulting in a remarkable 86% biodiesel yield at the given reaction circumstances. Additionally, the decrease in biodiesel generation with the increase the loading over 3%, might perhaps be ascribed to an overabundance of heterogeneous catalysts inside the reaction vessel. The excess of catalysts may impede the efficient combination of reactants, leading to a decrease in the total production of biodiesel. Greater catalyst loadings may also result in mass transfer limitations for reactants and products, both of which may contribute to suboptimal biodiesel synthesis. Furthermore, an increase in the viscosity of the reactant mixture can impede the mixing and mass transfer processes, ultimately leading to a decrease in biodiesel yield.

Effect of reaction temperature

The acceleration of the reaction rate was facilitated by the increased nucleophilic sites produced by the movement and diffusion of reactant molecules caused by the increase in reaction temperature. However, as the reaction temperature continued to rise, there was may an excessive evaporation of ethanol, resulting in a reduction in the yield of biodiesel.

Fig. 6 shows how the reaction temperature affects the creation of ethyl ester biodiesel. A rise in temperature enhances the substrate's ascension over the activation energy barrier[15]. The output of biodiesel normally improves with reaction temperature due to the reduced viscosity of date seed oil[16].At a reaction temperature of 80°C, biodiesel production reached 85% of its maximum. Reaction temperatures below or above 80°C resulted in reduced biodiesel production. Insufficient mixing among the reactants occurs due to the high viscosity of the oil at lower temperatures, which is caused by an inadequate reaction temperature. The enhancement of the biodiesel production does not occur when the reaction temperature is raised above 80°C. Ngige and colleague[17] found that raising the reaction temperature causes a faster rate of saponification and polarity is recognized as a factor that contributes to the restricted generation of biodiesel at high reaction temperatures. In addition, Baskar *et al.*[18] reported a decrease in the polarity of ethanol as a consequence of the excessive heating of reactants during a transesterification step. The diminished polarity is recognized as a contributing element to the constrained generation of biodiesel at high reaction temperatures.

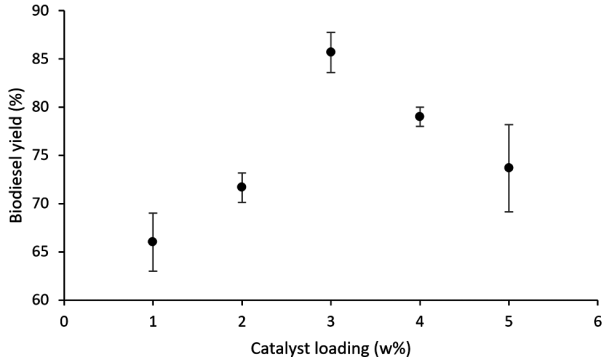

Fig. 5 — Effect of the concentration of the catalyst on biodiesel yield (%). Reaction conditions: ethanol to date seed oil ratio of 10:1, reaction time 3 h, and reaction temperature of 80°C

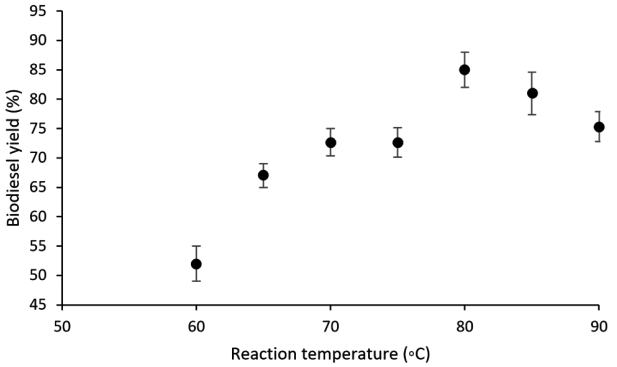

Fig. 6 — Effect of reaction temperature on biodiesel yield (%) at reaction conditions: catalyst loading 3 wt%, ethanol to date seed oil molar ratio 10:1, 3 h

Effect of ethanol-to-oil molar ratio

Several research studies have established that the molar ratio of triglyceride to alcohol is a critical determinant in the quantity of biodiesel that can be generated[12]. In order to produce one mole of glycerol and three moles of fatty acid ester, the transesterification process theoretically requires the coupling of one mole of triglyceride with three moles of alcohol. However, due to the reversible nature of the reaction, a substantial amount of alcohol is utilized to drive the reaction in the desired direction, thereby yielding a greater quantity of ester conversion in a significantly shorter amount of time. A molar ratio of 3:1 was employed initially in this experiment; subsequently, this ratio was increase from 3:1 to 12:1. The factors contributing to the variability in biodiesel production when the molar ratio is altered are highlighted in Fig. 7. The observed outcome of altering the ratio from 3:1 to 10:1 was a notable augmentation in the generation of biodiesel. Nevertheless, further increasing the ratio did not provide a commensurate rise in biodiesel output. Furthermore, it has been discovered that an excessive quantity of ethanol leads to an increase in the concentration of soluble glycerol in biodiesel. This excessive concentration of glycerol as a solute might potentially impede the separation process of biodiesel. This observation might perhaps be attributed to the presence of an excessive quantity of alcohol inside the solution.

Effect of reaction time

Given the direct correlation between energy consumption and time in the biodiesel synthesis process, it is essential to ascertain an appropriate response time. In order to investigate the impact of reaction time on the percentage of biodiesel yield, duration of the reaction was manipulated within the range of 1 to 5 h.

The initial yield of the reaction exhibited a significant increase when it was conducted for 3 h. This phenomenon might be attributed to the fact that reactants need a certain minimum duration to undergo a reaction, often referred to as the activation energy. A shown in Fig. 8, when the reaction time was increased from 3 to 4 h and subsequently to 5 h, the yield% decreased across all catalyst concentration and ethanol/oil ratio values. This drop may be attributable to the reversibility of the transesterification process. As a result, yield percentage decreases beyond the optimal threshold. The observed phenomenon may be attributed to the gradual decline in the quantity of active sites that are accessible over time, which occurs as a consequence of catalyst deactivation. A yield of 85% was achieved within a 3 h time frame, which may be seen as optimal in terms of cost-effectiveness and its relatively greater biodiesel production compared to other catalysts. In addition, the use of an extended reaction time may lead to the occurrence of saponification or the reverse reaction, resulting in a decrease in the conversion of waste cooking oil.

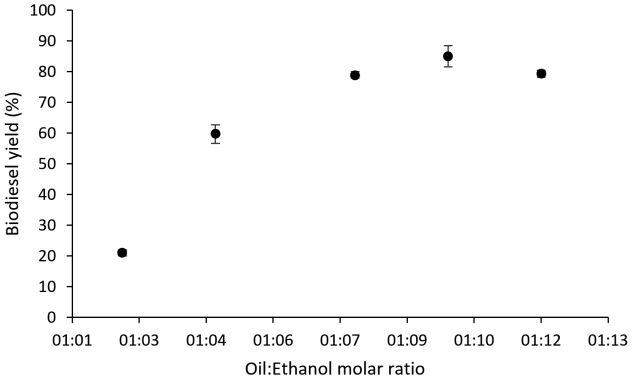

Fig.7 — Effect of ethanol to oil molar ratio on biodiesel yield (%) at Reaction conditions: catalyst loading 3 wt%, reaction time 3 h, reaction temperature 80℃

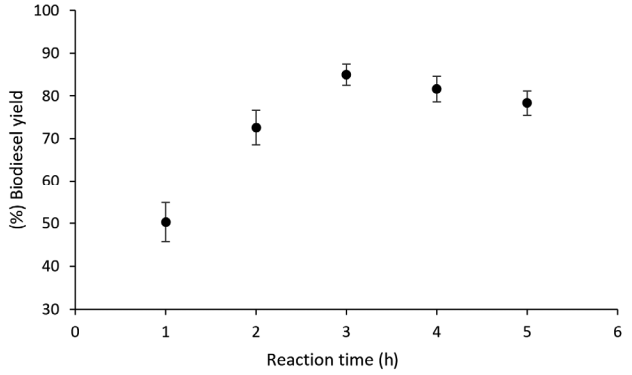

Fig. 8 — Effect of reaction time on biodiesel yield (%). Reaction conditions: catalyst loading 3 wt%, ethanol to date seed oil molar ratio 10:1, and reaction temperature 80℃

Table 6 — Biodiesel's fuel qualities at ideal reaction circumstances

Property	Unit	ASTM	Measured value for prepared biodiesel
Density	kg/m^3	860-894	894
Viscosity @40 ◦C	mm^2/s	1.8-5.0	4
Acid number	mg KOH/g	≤ 0.45	0.7
Flash point	℃	>120	130

Characteristics of Produced Biodiesel

The fuel qualities of the produced biodiesel were analyzed according to the American fuel standards of ASTM, as shown in Table 6. These parameters

include density, flashpoint, kinematic viscosity and acid value. The data shown in Table 6 demonstrates that the biodiesel generated exhibited fuel properties of superior quality, falling within the specified range outlined by the biodiesel standard.

Conclusion

The study showed that Pegnum harmala plant has the potential to be a new catalyst for producing biodiesel, resulting in an 85% output of biodiesel. This technique demonstrated an eco-friendly and sustainable strategy to producing biodiesel by using a readily accessible biomass resource. Using waste cooking oil in this research shows potential for biodiesel generation. This is crucial because of the current environmental issues and the decreasing stocks of petroleum-based fuels, which provide major difficulties to the progress and maintenance of human quality of life. The optimal reaction conditions for achieving the best productivity were identified as: a temperature of 80℃, a reaction period of 3 h, a molar ratio of ethanol to date seeds oil of 10:1, and a catalyst loading of 3%. Under these particular circumstances, a biodiesel production of 85% was achieved. An extensive research was done to test and assess the fuel qualities of synthetic fatty acid ethyl esters in regard to the established parameters defined in ASTM. Future study should focus on cost estimates, engine performance, and smoke emission reduction in the biofuel producing process.

Conflict of interest

The authors declare no conflict of interest.

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