

Research Article

Enhancing the Production Yield of Jatropha and Pongamia Oil-Based Biodiesel by Introducing Nanocatalyst

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Fossil fuel depletion, increasing demands of energy, and harmful emission production led to do research on biofuels. In this research, biodiesel is developed by blending of Jatropha and Pongamia oil with the help of magnetic stirrer-assisted transesterification process. Heterogeneous copper-doped titanium oxide catalyst was synthesized by wet impregnation method. The developed catalyst is characterized through XRD and HRTEM analyses and used to enrich the biodiesel yield and fuel properties, viz., viscosity, flashpoint, and fire point. The maximum yield of 90.2% is obtained with catalyst concentration of 3 wt%, reaction time of 3 hrs, temperature of 60°C, and methanol to oil molar ratio of 20:1.

1. Introduction

Worldwide depletion of fossil fuels, higher consumption of diesel, increasing environmental pollution, and higher usage of nonrenewable energy resources move the researchers towards sustainable development that promotes the significance of alternative fuel [1–3]. Among the alternative fuels, nonedible oils are preferred most owing to its economically low cost and its simplified processing. In India, nonedible oils such as Jatropha and Pongamia harvests are increased owing to its favorable climatic conditions and its potential to grow at water-scarce areas. Further, these oils are free from fatty acid content that makes them to be suitable for producing biofuel. Previous research augmented that biofuel extract from fat and vegetable oils has better cetane rating while compared with conventional fuel. Likewise, these biofuel consist of higher oxygen content that leads to better combustion [4–6]. The main drawback in biofuel extraction is poor yield from their raw substance. In general, transester-

ification process is normally adopted by the research for biofuel synthesis with the help of catalyst which might be base or acidic. Generation of more waste water and difficulties in catalyst separation from biodiesel are two major limitation in base catalyst [7, 8]. In order to overcome these limitations, heterogeneous catalyst is preferred by researchers since these are environmental friendly, easy for separation [9, 10], reusable, and noncorrosive [11, 12]. Metal oxide and carbon-based nanomaterials, viz., SiO₂, TiO₂, graphene, and MWCNT, have excellent properties such as stability, insolubility, and recyclability that can be used for development of biofuel. Likewise, higher surface area and lower particle size of nanocatalyst help to improvise the yield of biodiesel extraction [13–16]. Among the available catalyst, titanium dioxide- (TiO₂-) based catalyst has better capability to catalyze the esterification and transesterification process for biodiesel production, and it can be easily separated from the reaction mixture for further use. Titanium-based catalyst synthesis is economically feasible that increases the

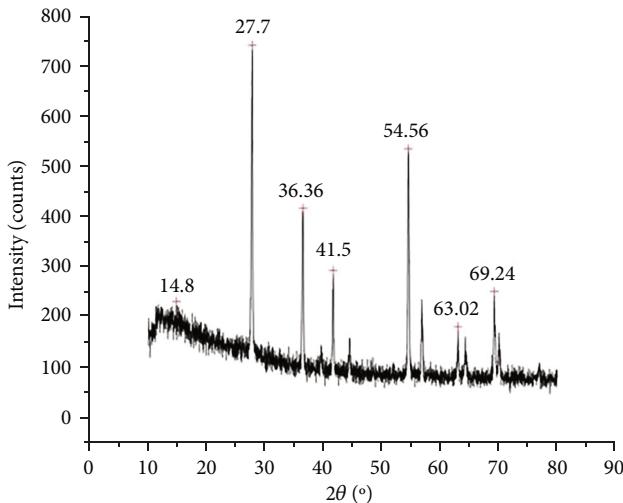


FIGURE 1: XRD of prepared catalyst.

possibility of low-cost biodiesel extraction [17–19]. Herein, research based on TiO_2 performance on biofuel depicts that doping or composting of metal oxide or metal nanoparticles improvise the yielding performance of biofuel. Maximum yield of 90.5% was obtained when Pongamia oil is used as a feedstock biodiesel with nanocatalyst transesterification process under optimal condition of 3% catalyst loading (*w/w*), 12:1 methanol to oil molar ratio, and 60°C temperature [20]. For Jatropha oil with nanocatalyst, the maximum yield of biodiesel 93% was obtained with optimal parameters like time of 3 hrs, temperature of 57.5°C, catalyst concentration of 7 wt%, and methanol molar ratio of 1:10 [21], and for mixed vegetable oil, maximum yield of 76% biodiesel is obtained with help of prepared catalyst under the following condition of 240 min reaction time, 20:1 methanol to oil molar ratio, 80°C temperature, and catalyst concentration of 7 wt% [22–26].

Based on clear-cut literate survey, it can be noted that the yield of biodiesel production can be increased by maintaining optimum level of various parameters like time of reaction, temperature of reaction, methanol to oil molar ratio, and catalyst. Likewise, addition of nanocatalyst improvise the yield of biodiesel. However, efficiency of doped nanocatalyst was rarely reported. Likewise, efficiency of nanocatalyst for dual-blended oil was not yet reported. Hence, in this research, an attempt has been to understand the effect of copper-doped TiO_2 as nanocatalysts on yielding efficiency on dual-blended Jatropha and Pongamia oils. Copper-doped TiO_2 nanoparticles were synthesized by wet impregnation method, and transesterification process was adopted to extract biodiesel from dual-blended oil, viz., Jatropha and Pongamia oils.

2. Materials and Method

Titanium dioxide (TiO_2) and cupric sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were purchased from Merck in India with purity of 98%. Jatropha and Pongamia oils are purchased from Coimbatore local market, and it is used without any further purification.

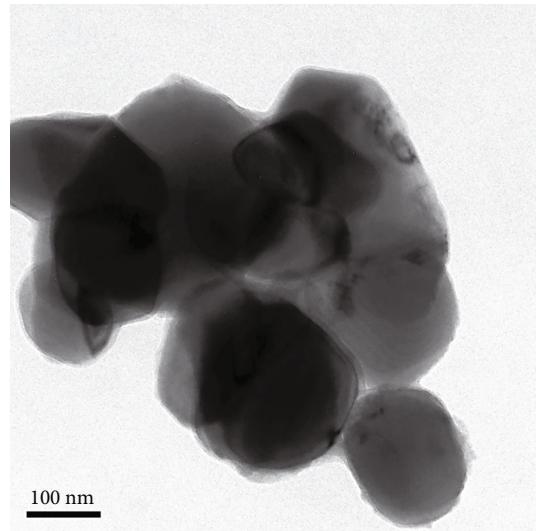


FIGURE 2: HRTEM of prepared catalyst.

Methanol (CH_3OH) with purity of 95% was supplied by Krishna Chemicals Limited, Tamil Nadu, India.

2.1. Synthesis of Cu-Doped TiO_2 . The Cu-doped TiO_2 nanomaterials were synthesized by using wet impregnation method [27]. Initially, the TiO_2 nanoparticles were mixed with calculated concentration of distilled water and added with 10 wt% of aqueous cupric sulphate solution, followed by stirring at 1250 rpm up to one hour with the help of hot plate coupled magnetic stirrer. The precursor was kept in hot air oven at 150°C to remove the water content. The dried concentrated powder was calcinated at 550°C for 5 hrs with furnace cooling.

2.2. Transesterification Process of Biodiesel. The reaction was carried in a 250 ml flat bottom flask, and the constant temperature of reaction was maintained keeping the flask under oil bath. The reaction setup is equipped with a magnetic stirrer (0 to 1500 rpm) with heater range of 0 to 100°C, coupled with condenser to reduce the vaporization of methanol during reaction, and a thermometer was utilized to measure the reaction temperature. Throughout, the experiment stirrer speed was maintained at 800 rpm. Jatropha and Pongamia oils were mixed at equal ratio for production of mixed oil biofuel. The reactor catalyst concentration (1, 3, 9, and 12% *w/w*), oil to methanol ratio (10:1, 15:1, 20:1, and 25:1), temperature (40, 50, 60, and 70°C), and reaction time (1, 2, 3, and 4 hrs) varied during the transesterification reaction. Finally, after the reaction, the biofuel was separated using separating funnel. The yield of biodiesel produced was calculated by the following equation.

$$\text{Yield of biodiesel (\%)} = \frac{\text{Weight of biodiesel produced}}{\text{Weight of oil}} \times 100. \quad (1)$$

TABLE 1: Properties of the biodiesel.

Catalyst	Density (kg/m ³)	Kinematic viscosity (m ² /s)	Flash point (°C)	Fire point (°C)	Diesel index	Cetane number
KOH	848	0.0212	61	68	34.22	34.28
CuTiO ₂	776	0.0114	65	71	47.16	44.91

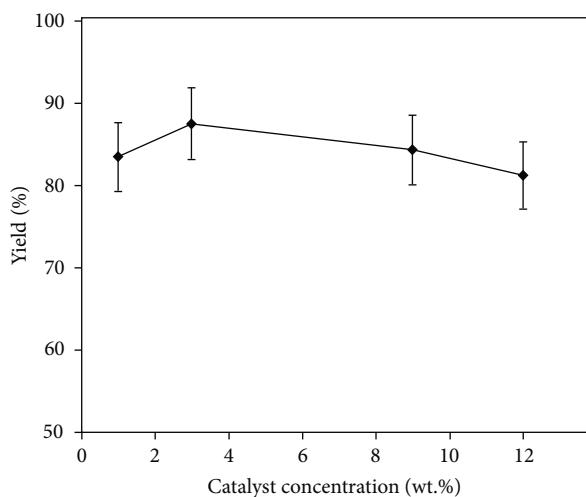


FIGURE 3: Variation of yield based on catalyst concentration.

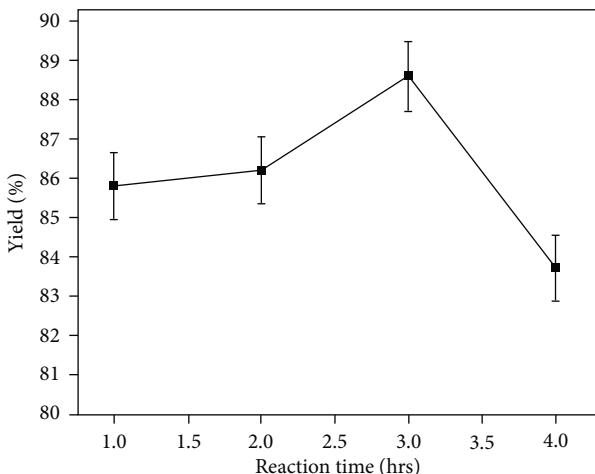


FIGURE 4: Variation of yield based on reaction time.

3. Results and Discussion

3.1. Characterization of Nanoparticles. Surface morphology and particle size of the CuTiO₂ nanoparticles were analyzed with the aid of HRTEM. Phase evaluation and particle confirmation of synthesized nanocatalyst were investigated by powder X-ray diffraction (XRD). The obtained XRD patterns of TiO₂-copper-added nanocatalyst confirm the hexagonal copper formation and tetragonal TiO₂. The attained patterns matched with JCPDS nos. 89-1397 and 89-6975. It represents that copper and TiO₂ were clearly mixed in the form of hexagonal and tetragonal crystallites of produced

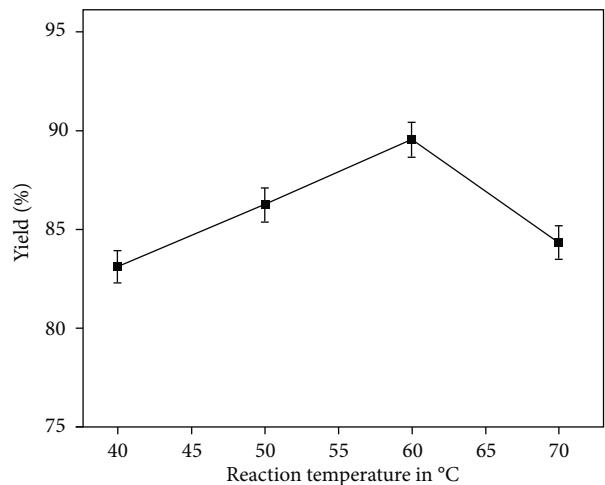


FIGURE 5: Variation of yield based on reaction temperature.

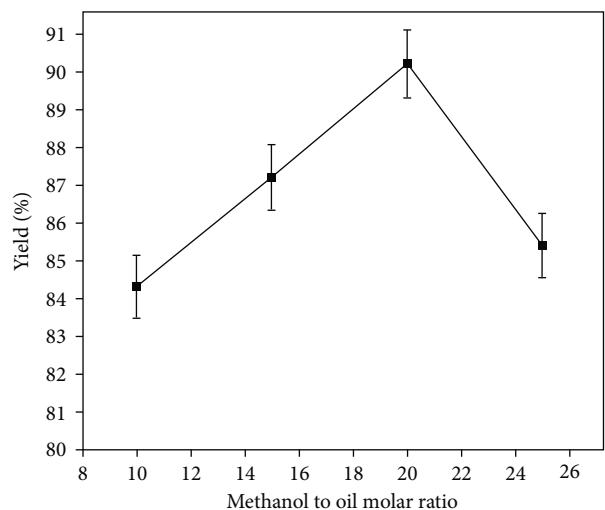


FIGURE 6: Variation of yield based on methanol to oil molar ratio.

nanoparticles. The attained XRD pattern and the obtained peaks are depicted in Figure 1.

High resolution transmission electron microscopy (HRTEM) is an imaging mode of the transmission electron microscope (TEM) that allows for direct imaging of the atomic structure of the sample. The prepared sample was analyzed using HRTEM, and the size of the nanomaterial was measured as ~100 nm as shown in Figure 2. The copper particles were adsorbed on the surface of titania, which is evident from the distinct coloration at the outer periphery.

The biodiesel properties such as viscosity and density are measured and compared with homogeneous (KOH) and heterogeneous (CuTiO₂) catalyst. When compared with both, the catalyst CuTiO₂ reduces the kinematic viscosity of biodiesel. Better surface area of catalyst leads to improvement in the quality of biodiesel yield and also influences band gap energy during transesterification; it enhances the catalytic activity. Other essential properties of biodiesel such as flash and fire point are evaluated and listed in Table 1.

TABLE 2: Comparative table for proposed research.

Sl no.	Oil	Catalyst	Yield (%)	Reference
1	Jatropha	ZnO-CaO	98.2	[41]
2	Neem oil	Cu doped ZnO	73.95	[42]
3	Waste cooking oil	Cu doped ZnO	97.71	[43]
4	Waste cooking oil	TiO ₂ /PrSO ₃ H	98.3	[44]
5	Jatropha and Pongamia oils	Cu@TiO ₂	90.2 (present work)	—

3.2. Effect of Nanocatalyst Concentration. The transesterification reactions of Jatropha and Pongamia mixed oil were performed with the help of CuTiO₂ nanocatalyst by varying its concentration from 1 to 12 (Figure 3). Herein, three parameters are maintained constant such as reaction time of 3 hrs, temperature of 60°C, and methanol to oil molar ratio of 15:1. From Figure 3, it can be identified that the higher yield percentage is attained at 3 wt% concentration of nanocatalyst. Further increase in the concentration of nanocatalyst results in the decrement in the yield of biodiesel. When the catalyst concentration is increased, interaction among the catalyst and methanol increases that promotes number of active sites up to 9 wt% [28, 29]. Further increase in mass ratio (10 wt%) decreases the biodiesel conversion yield percentage due to reactant high viscosity and high resistance of mass transfer [30, 31].

3.3. Effect of Reaction Time. The reaction period was an important parameter to study the behavior of transesterification biodiesel yield. The experiment time range was studied from 1 hr to 4 hrs where other three parameters catalyst concentration 3 wt%, temperature 60°C, and methanol to oil molar ratio 15:1 maintained as constant. Biodiesel production yield was increased up to 3 hrs at 88.6% after that yield reduces due to reduced activities of catalyst [32] as illustrated in Figure 4. During reaction after 3 hrs, high immiscibility occurs between Jatropha and Pongamia mixed oil with added methanol. So, the biodiesel yield was reduced after 3 hrs of reaction [33, 34]. In the liquid phases during reaction, immiscibility problem should be avoided by longer reaction time to enrich the biodiesel conversion rate [35, 36].

3.4. Effect of Reaction Temperature. Temperature of reaction was varied from 40°C to 70°C to find out the optimized value for higher biodiesel yield. Other parameters catalyst concentration 3 wt%, time 3 hrs, and methanol to oil molar ratio 15:1 maintained as constant. From Figure 5, it is noted that maximum yield was obtained up to 60°C, and it decreases due to various factors. Specifically, the transesterification reaction involved is endothermic, and however, increase in temperature lowers the viscosity of oil and it increases the rate of mass transfer thus improving the mixing properties [37]. One more important factor to be considered is vaporization of methanol that affects the yield during the transesterification process [38]. Optimal temperature of this condition was found to be 60°C.

3.5. Effect of Methanol to Oil Molar Ratio. The effect of methanol to oil molar ratio in CuTiO₂ involving reaction

was studied from 10:1 to 25:1, and the results are depicted in Figure 6. Other parameters maintained as catalyst concentration 3 wt%, time 3 hrs, and temperature 60°C. In this reaction, optimal methanol to oil molar ratio is 20:1, and at this condition, maximum yield obtained is 90.2%. Methanol addition to transesterification process is an important parameter because triglyceride is a reversible reaction which happens if sufficient methanol is not supplied. Appropriate ratio of methanol leads to forward direction of equilibrium to get the higher yield of biodiesel [39].

Higher volume content of methanol or molar ratio after 20:1 leads to decreases in the biodiesel yield due to methanol deactivation of the products, dilution of oil, and glycerol byproduct dissolving with excess content of methanol [40]. The comparison table for the proposed research is illustrated in Table 2.

Reusability of the synthesized nanocatalyst was measured after drying the catalyst that are collected from reaction mixture. At stage one, ~70% of biodiesel was produced, followed by ~61% on second stage; further, 52% of biodiesel yield was produced at the final stage. The residuals can be blended with diesel; this fact helps in decreasing usage of fossil full and promotes ecofriendly sustainable environment.

4. Conclusion

Biodiesel production with the help of transesterification reaction was investigated using heterogeneous nanocatalyst (CuTiO₂). The different parametric condition was carried out in this research from overall reaction; the maximum biodiesel yield obtained was 90.2%. The optimized time of reaction is 3 hrs, methanol to oil molar ratio is 20:1, temperature is 60°C, and 3 wt% of catalyst concentrations. Biodiesel physicochemical properties were also studied in order to identify particle confirmation of nanocatalyst. From the overall analysis, CuTiO₂ can be used as the heterogeneous nanocatalyst for biodiesel transesterification process when feedstock is vegetable oils. Usage of these biofuels helps in decreasing the usage of fossil fuels that promote ecofriendly environment.

Data Availability

Data are available upon request from the author.

Conflicts of Interest

The authors declare no conflict of interest.

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