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Dolomite as A Potential Source of Heterogenous Catalyst for Biodiesel Production from *Pongamia pinnata*

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ABSTRACT

Biodiesel production from *Pongamia pinnata*, a tree-based oil using healthcare industrial waste dolomite as a catalyst, was studied. The studies aimed to establish the ideal parameters for producing biodiesel, such as temperature, the ratio of methanol to oil, and the weight percentage of the catalyst. The healthcare industrial waste was procured and characterized. With the operating conditions, temperature maintained at 75°C, methanol to oil molar ratio of about 20:1, and a catalyst weight of 5%, the optimum yield of 92.3% was obtained. The tree-based nonedible oil source for biodiesel production was suggested widely due to its ability to achieve sustainable development goals (SDGs). The *Pongamia Pinnata* cultivation on barren land supports the afforestation projects with economic and environmental values; further biodiesel from renewable bioresources reduces emissions, and livelihood development to eradicate unemployment are the primary objectives for achieving the SDGs. The tree-based biodiesel production and adaptation of dolomite as a heterogeneous catalyst have proven to be a recent attraction among scientists. The present study is the first report on *Pongamia pinnata* for biodiesel production catalyzed by dolomite.

INTRODUCTION

The ability to produce energy scales the development of the nation. Resource depletion, pollution due to emissions, and global governance's commitment to climate change are pushing to shift the fossil fuel-based energy production process into renewable energy sources (Dey et al. 2022). The capital investment toward infrastructure, time consumption, inconsistency in power generation, and other parameters limit energy production from renewable sources like wind, solar, and tide. Locally produced biofuel from domestic resources mitigates transboundary emissions and favors social welfare. Biodiesel from vegetative sources is widely investigated and adopted as an alternative to fossil fuels. As evidenced by the performance and emission studies, biodiesel significantly reduces air pollution in the production and operation processes (Mac Kinnon et al. 2018).

Positive socioeconomic effects from the production and use of biodiesel as an alternative fuel may eventually result in sustainable development. Developing biodiesel can yield socioeconomic benefits for rural communities and agricultural sectors, and this livelihood development significantly contributes to achieving the SDG, among other sustainability credits (Brinkman et al. 2020). However, the large-scale production of fuel-yielding crops seriously threatens food security due to the land use pattern. Accordingly, the search for biodiesel feedstock shifted toward non-edible sources.

As a sustainable energy source, biodiesel helps reduce greenhouse gas emissions, which is part of the REDD+ (Reducing Emissions from Deforestation and Forest Degradation) program. Through REDD+, developing countries will be encouraged to manage their forests responsibly and prevent further global warming. In comparison to fossil fuels, biodiesel is a greener fuel that can be generated from renewable resources like plant or animal fats, which lowers emissions from vehicles. Biodiesel production from wild vegetation sources further strengthens the implementation of REDD+, and this further facilitates the climate financing from developed countries to develop forest regions in developing countries (Kuh 2018). The potential of various tree-based oils from *Azadirachta indica*, *Jatropha curcas*, *Madhuca longifolia*, *Pongamia glabra*, *Calophyllum inophyllum*, *Pongamia pinnata*, *Hevea brasiliensis*, *Simmondsia chinensis*, *Linum usitatissimum* were studied (Chimezie et al. 2022).

The monotypic genus Karanja is a known species native to Southeast Asia and the Indian subcontinent. Pongamia is a nitrogen-fixing, self-pollinating tree that grows well in humid, subtropical climates with minimum mean monthly temperatures between 10 and 50°C. It may also be grown easily in wastelands and infertile areas where temperatures range from 16 to 40°C for ideal growth (Sharma et al. 2020).

The United States and other regions with humid tropical climates have adopted this plant. Pongamia trees can generally attain a height of 15-25 m, begin to flower at 3-4 years old, achieve maturity in 4-5 years, and yield up to 90 kg of seeds annually. The wood, seeds, and leaves from Pongamia trees have various value-added applications. For alternative biomass sources, *Pongamia pinnata* has numerous benefits. Primarily, it is a resilient and drought-tolerant tree that can flourish in a variety of soil conditions, such as marginal and degraded areas, making it appropriate for cultivation in drought-prone regions where other crops could find it difficult. The second reason is that *Pongamia pinnata* is a nitrogen-fixing plant. It works in symbiotic partnerships with bacteria to enrich the soil with nitrogen, which lowers the demand for external fertilizers and increases soil fertility. Some of these applications include fuel, livestock feed, and medicinal uses (Degani et al. 2022).

The most common biodiesel production from bio-oil involves the transesterification process; a catalyst facilitates the reaction between the feedstock of vegetable oil and short-chain alcohol during the transesterification process. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are two homogeneous base catalysts that are frequently employed to catalyze the transesterification of refined vegetable oil (Amirthavalli et al. 2022). When employing crude vegetable oil feedstock with a high free fatty acid (FFA) content, soap production is unavoidable with the base catalyst, and this limitation mandates the pretreatment of high FFA content feedstock using homogenous acid catalysts like phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4) to lower the FFA concentration (Baskar et al. 2019).

However, using a homogenous catalyst has always been linked with drawbacks, including the inability to separate homogeneous phase products, the fact that they are non-recyclable, and the significant increase in the cost of using a wastewater treatment system to neutralize the catalyst before discharging. The enzyme catalyst is expensive to replace the homogeneous. Recyclable and readily separable, heterogeneous catalysts have emerged as a viable substitute for homogeneous catalysts, offering better performance (Brahma et al. 2022).

Dolomite is a sedimentary rock that occurs naturally and includes carbonates of magnesium and calcium. To make biodiesel, transesterification is a process that it catalyzes. Initi0ally, the ions calcium and magnesium function as Lewis acid sites to accelerate the reaction and act as catalysts. Due to its broad availability, dolomite is also less expensive than the other catalytic substitutes (Maroa & Inambao 2021).

It uses less energy to make and generates less waste because of its capacity to regenerate and reuse itself. Furthermore, studies show that dolomite catalysts outperform other catalysts in terms of yield and reaction kinetics. Dolomite from industrial waste in the healthcare sector has special advantages for the manufacture of biodiesel since it may be used for both environmental remediation and catalysis. When dolomite from medical waste is used, resource usage is streamlined, lessening the impact on the environment and solving disposal issues. Moreover, the inherent catalytic activity of dolomite promotes effective transesterification processes, increasing the yield of biodiesel. This strategy adheres to the circular economy principles by reducing waste and promoting the creation of renewable energy.

The present study is the first work investigating the use of dolomite in the transesterification of Karanja oil with a higher yield of biodiesel. The current work uses Response Surface Methodology (RSM) to optimize the transesterification parameters for the methyl ester synthesis from *Pongamia pinnata* seed oil. This study examined how process variables, including catalyst weight, temperature, and the ratio of methanol to oil, affected the amount of biodiesel produced. The ASTM technique was used to determine the characteristics of *Pongamia pinnata* biodiesel.

MATERIALS AND METHODS

Materials

Pongamia pinnata oil was obtained from the highway road of Bahour main road, Puducherry (11˚48.56.5"N, 79˚4501.4" E) (Fig. 1). The seed extracted *Pongamia pinnata* oil was found to have the density of 906 kg/m^3. At 40°C, the oil's viscosity was estimated as 26.5 mm^2/s. The oil had an acid value of 7 mg KOH/g. Stearic acid (18.36%), linolenic acid (14.87%), oleic acid (54.22%), and palmitic acid (12.55%) make up the fatty acid makeup of *Pongamia pinnata* oil. The dolomite was obtained from Puducherry, the healthcare sector of TTK, Puducherry.

Transesterification Process

Every transesterification experiment was carried out in a 50 ml vial. 20 grams of Karanja oil were combined with a 3:1 methanol to oil ratio, 1 weight percent catalyst, and a temperature of 70°C sustained for 9 h at 400 rpm. To

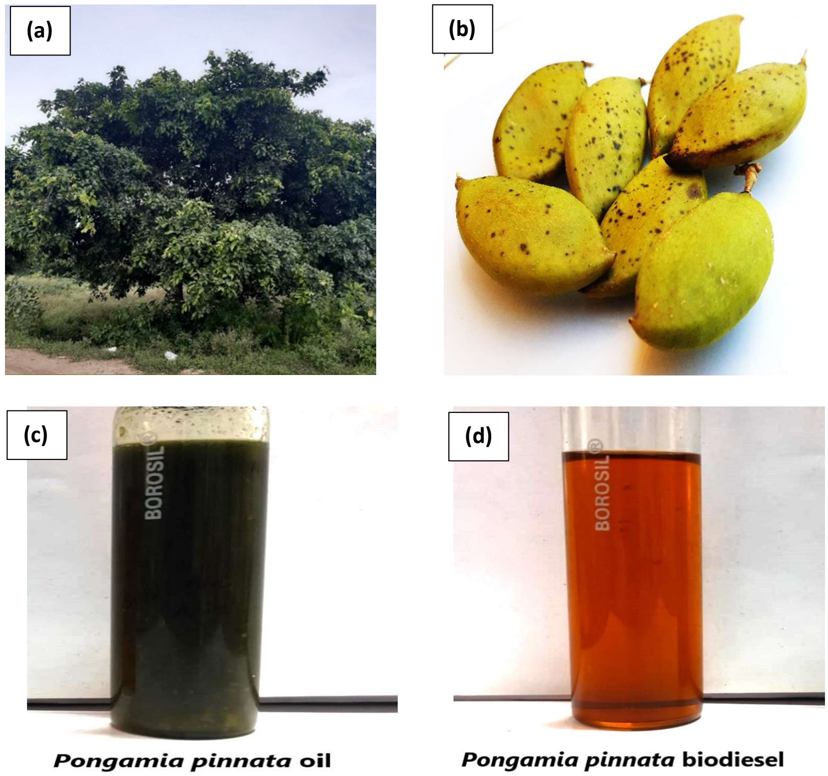

Fig. 1: *Pongamia pinnata* Linn (a) Tree (b) Seed (c) *Pongamia pinnata* oil (d) *Pongamia pinnata* biodiesel.

eliminate any remaining methanol in the combination, the sample was centrifuged at 4000 rpm after 9 h. Methanol to oil ratio of 15:1 to 25:1, a temperature range of 65°C to 85°C, a catalyst weight of 1 to 3 wt%, and methyl esters yield measured by GC-MS were all adjusted to maximize production (Fig. 2). Gas chromatography-mass spectroscopy (CLARUS 500, PerkinElmer, USA) was used to analyze the biodiesel made from the Karanja oil (*Pongamia pinnata*). Every experiment was carried out in triplicates (Vishali et al. 2023).

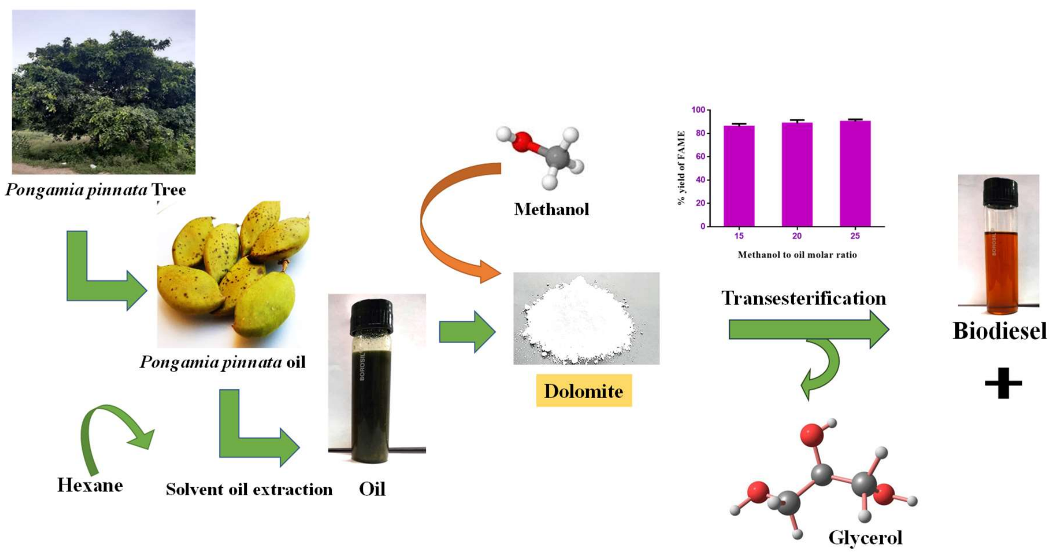

Fig. 2: Process flow for biodiesel production from *Pongamia pinnata* oil.

Biodiesel yield = (Mass of biodiesel produced/ Mass of oil used) × Area % of FAME × 100

Characterization

Pongamia pinnata biodiesel produced using a dolomite catalyst has been subjected to GC-MS analysis. A potent method for characterizing biodiesel is gas chromatography-mass spectrometry (GC-MS) analysis, which yields comprehensive data on the composition and quality of biodiesel fuels. Gas chromatography is used in this analytical approach to separate the components of biodiesel according to their volatility and affinity for the stationary phase. Mass spectrometry is used to identify and quantify these components by examining their mass-to-charge ratios.

RESULTS AND DISCUSSION

Effect of Methanol Content

Stoichiometry indicated that three moles of methanol were needed for the transesterification reaction to yield methyl esters from one mole of triglyceride. Excessive addition of alcohol can be used to adjust the rate of reaction. The stoichiometric molar ratio of alcohol to oil in the generation of biodiesel is 1:3; however, to shift the chemical equilibrium in favor of the generation of biodiesel, more excellent molar ratios are a convenient solution. Furthermore, developing the three phases (oil, alcohol, and catalyst) at the start of the reaction may limit the contact between the reactive mixes; still, in this scenario, the excess alcohol in the reaction reduces the issue (Hoda 2010). As shown in Fig. 3, biodiesel yield improves with increased methanol-to-oil ratio up to a certain point when the yield declines from the highest possible biodiesel production. Therefore, it is essential to carefully optimize the methanol-to-oil ratio to achieve maximum biodiesel yield without compromising efficiency and cost-effectiveness (Kedir et al. 2023). The highest yield of 90.7% was obtained at a 20:1 methanol to oil molar ratio.

Effect of Temperature

The temperature significantly influences biodiesel production via transesterification since the intrinsic rate constants strongly depend on temperature. Therefore, to get the highest yield, it is crucial to adjust the operating temperature. The trials were performed with a temperature range of 65°C to 85°C to obtain the optimum yield (Takase 2022). The data shown in Fig. 4 indicates that biodiesel yields rise as the temperature rises, peaking at 75°C, after which it begins to fall. After 75°C, the conversion percentage decreased. As the temperature rises, the methanol vaporizes at a greater temperature, shifting the balance to the reactant side and decreasing the biodiesel output (Ezekannagha et al. 2017).

Catalyst Concentration

The impact of catalyst amount (range of 3-5 wt%) in the transesterification reaction as catalyst was shown in Fig. 5. The percentage yield of 84.6% was obtained at 3wt% catalyst concentration. Further increased the catalyst concentration to 4 wt% the maximum yield of 92.3 was obtained. When the amount of catalyst is increased beyond 4 wt%, the yield of biodiesel decreases to 88.3%. This may be due to too high concentration of catalyst reduces the reactant interaction and also favors high glycerin concentration which in turn reduces the biodiesel yield (Jan et al. 2023).

Reusability of Dolomite

Dolomite catalyst's reusability was also looked at since it can lower process costs. Following the reaction, the dolomite catalyst was filtered out and reused for a new reaction

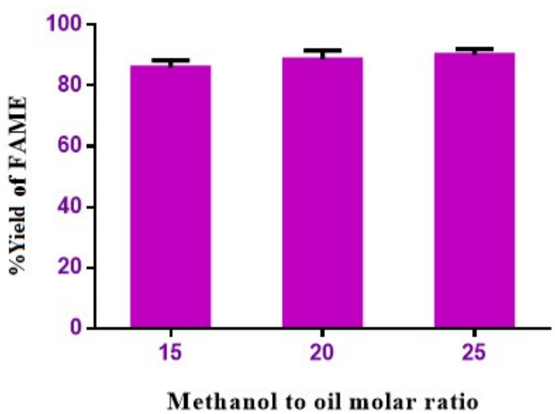

Fig. 3: Effect of methanol to oil molar ratio (15:1, 20:1, 25:1) on *Pongamia pinnata* biodiesel production.

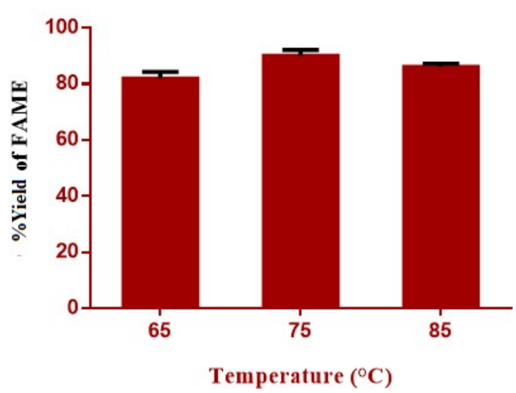

Fig. 4: Effect of temperature (T = 65, 75, and 85°C) on *Pongamia pinnata* biodiesel production.

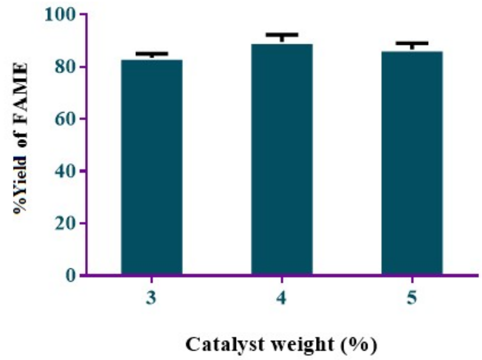

Fig. 5: Effect of catalyst concentration (3, 4, and 5 wt%) on *Pongamia pinnata* biodiesel production.

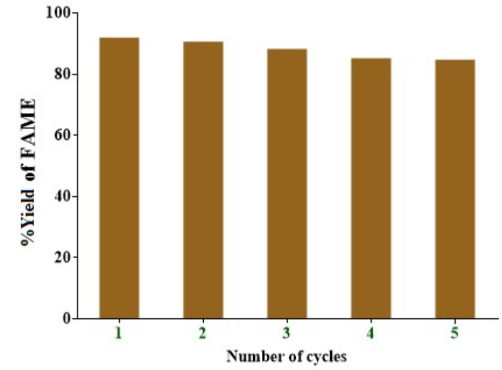

Fig. 6: Reusability studies of dolomite catalysis on *Pongamia pinnata* biodiesel production.

(Fig. 6). With a 4 weight percent catalyst quantity and a 20:1 molar ratio of methanol to oil, the transesterification process was conducted at methanol reflux. From Fig. 4 there was no appreciable reduction in the biodiesel yield. The reduction in the yield after the five cycles of recycling of the catalyst was found to be 7.79% (Ilgen 2011).

Characterization of Biodiesel

GC-MS analysis of the product revealed the presence of several significant compounds (Fig.7). Octadecenoic acid (Z)-, methyl ester was discovered with a retention duration of 54.98 minutes, indicating its presence in the sample. In addition, it was found that methyl stearate had a retention duration of 3.96 minutes, but the methyl ester of hexadecanoic acid had a retention time of 2.54 minutes. These compounds are significant because feedstock used to produce biodiesel typically includes them and because they are critical to the fuel's quality and properties. Accurate identification and measurement of these components provide crucial information for determining the sample's general composition and suitability for biodiesel production.

CONCLUSIONS

The findings of the research emphasize the significant effects of temperature, catalyst concentration, and methanol to molar ratio on the production of biodiesel from *Pongamia pinnata* oil. To produce biodiesel with improved quality and yields and to support environmentally friendly and sustainable energy production, the study emphasizes the importance of optimizing these factors. An industrial waste dolomite heterogeneous catalyst is used for biodiesel production. Maximum biodiesel yield of 92.3% was observed at 20:1 methanol to oil ratio, temperature of 75°C, and catalyst weight of about 5 wt%. Additionally, research has been done on the catalyst's reusability. Even after five cycles, it has been discovered that dolomite still exhibits superior catalytic activity. The characteristics of the biodiesel made from *Pongamia pinnata* and diesel appear to be comparable.

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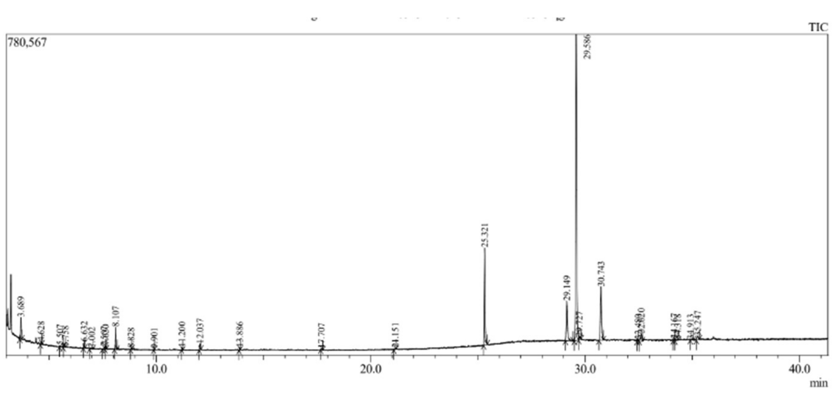

Fig. 7: GC-MS analysis for the produced *Pongamia pinnata* biodiesel.

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