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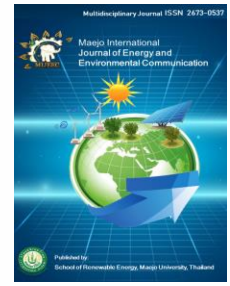

ARTICLE

Biomass-derived nano-catalyst for biodiesel production from waste cooking oil

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A B S T R A C T

This study aimed to produce a nanocatalysts from inexpensive barley straw using nickel (Ni) and cobalt (Co) to support waste cooking oil-based biodiesel production. At 400 °C without oxygen and 1-5 bars of pressure, the gasification procedure of barley straw biomass (100g dry basis) was utilized in a muffle furnace with Ni and Co nano-catalysts. The biomass:Ni:Co catalyst mixing ratio is 1:1:1. The catalyst content and reaction time were applied for 2 hours. Then, at molar ratios of methanol:oil (6:1, 9:1, and 12:1) with the amount of catalyst (1, 2, and 3% weight percent basis), at 2 hours reaction time. Accordingly, the factors impacting the transesterification of biodiesel synthesis were evaluated. The process employing methanol:oil molar ratio of 6:1 and a catalyst quantity of 2% wt was the best for producing biodiesel. Based on the results of this study, nanocatalysts formed from biomass, which can be obtained from agricultural waste, hold commercial promise as a catalyst source for biodiesel.

1. Introduction

Demand for energy on a global scale has increased, necessitating more use of fossil fuels. However, this energy source is finite and comes with serious pollution issues (Vu et al., 2018). A huge percentage of the energy used in the world comes from fossil fuels (oil, coal, natural gas), and refined oil is the type of energy that receives the most attention (Ramaraj & Unpaprom, 2016). Further analysis of the 2020 energy consumption statistics revealed that transportation, industrial, and other economic sectors had higher CO_2 emissions than the previous year. The highest amount of CO_2 emissions was from refined oil (Bhuyar et al., 2021). All sectors were affected by the increase in energy consumption. At present, energy is an essential component of human life and also plays an essential role in the growth of nations (Khunchit et al., 2020). For example, oil is the primary source of energy that is utilized in Thailand (Unpaprom et al., 2021).

In addition, oil is utilized for power generation in the agriculture sector, particularly in the industrial and transportation sectors (Ramaraj & Unpaprom, 2019a). However, given the circumstances that now exist, the price of oil is subject to constant change. Despite the increase in population and the rapid expansion of numerous industries, the demand for petroleum has not ceased growing, which runs counter to these trends (Ramaraj & Unpaprom, 2019b). As a result, the reserves of the rest of the world are decreasing due to the amount of oil. This includes the value of refined oil used over 50% (Saengsawang et al., 2020). It is known as diesel fuel consumption. Because the import volume is greater than the export volume, the finished oil consumption values (Manmai et al., 2021). The increase in import value was 12% more

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than last year when we consider the proportion.

They are most commonly utilized to produce thermal energy, which accounts for sixty percent of all applications of renewable sources of energy. The lack of fuel in Thailand can be alleviated by using biofuel (Dussadee et al., 2016; Van Tran et al., 2020). Its goals are to boost domestic output by making greater use of renewable energy sources and to cut down on pollution. Also, look for ways to reduce the expenses of production (Khammee et al., 2021). As was previously mentioned, this will increase the availability of oil at more affordable prices.

Diesel fuel is the most energy-rich of all energy derived from refined oil. However, it also produces significant amounts of carbon dioxide. Therefore, it is essential to find alternative fuels that have the same characteristics as diesel oil to replace it (Bohlouli & Mahdavian, 2021). The output of biodiesel, also known as biodiesel, has been increasing. It results in a decrease in demand for crude oil. The study found that Thailand has seen a dramatic increase in biodiesel vehicles (Saetang & Tipnee, 2021). To meet the growing demand for renewable energy, the government developed a strategy to develop alternative energy sources and renewable energy and to reduce the environmental impact of manufacturing, and there are several things possible (Abdelhady et al., 2020). These include increasing the domestic supply of renewable energies, improving energy efficiency, and improving production technology performance.

Even though energy prices will not hinder Thailand's economy's long-term growth and development, it is vital to consider them (Pimpimol et al., 2020). Therefore, the government has prioritized developing, promoting, and researching renewable energy sources (Pradechboon & Junluthin, 2022). Both the private and public sectors are actively encouraging the use of renewable energy (Souvannasouk et al., 2021). They also encourage people to take part in training on renewable energy. Understanding current energy issues is critical. The future will see renewable energy use increase yearly while natural fuel use will decline (Whangchai et al., 2021). Biodiesel is a fuel that has been synthesized using a chemical process, and the process that is produced by a transesterification reaction (Transesterification). The esterification reaction (Esterification) and biodiesel production in a 2-step process (Bohlouli & Mahdavian, 2021). It results in a substance called either methyl ester or ethyl ester (Saengsawang et al., 2020).

Additionally, this depends on the type of alcohol used. Glycerol is produced by reacting with acids, bases, or enzymes as catalysts or byproducts (Ajala et al., 2020). Furthermore, this can be used to fuel most diesel engines as biodiesel. A base catalyst is used in biodiesel production through a transesterification reaction. It can be divided into two types: Type 1, a homogeneous catalyst (Homogeneous catalyst). Commonly, chemical catalysts such as potassium hydroxide and sodium hydroxide are used (Faruque et al., 2020). These catalysts produce high biodiesel yields. However, the separation of the catalyst at the end of the production process, the product requires more water to wash. This results in soap formation and a lower product yield. A heterogeneous catalyst is not homogeneously dissolvable with the substrate.

Using catalysts made from natural materials, such as calcium oxide, is common. It can be separated easily after the production process is completed (Saengsawang et al., 2020). It is also reused in biodiesel production without the need to go through the washing procedure. It helps to reduce soap occurrence, saves costs, does not cause corrosion, is environmentally friendly and has low properties. This approach allows biodiesel to be synthesized similarly to a homogeneous catalyst. This technology can be challenging because it requires a lot of energy, and the biofuels it produces are not very high quality. Nanomaterials can be used to increase the efficiency and quality of energy use. The world has been forced to find other energy sources due to economic, environmental, and security issues (Zhu et al., 2021).

Not many biochemical modifications can be used to make biomass more cost-effective (Pradechboon & Junluthin, 2022). This makes it necessary to optimize and develop biochemical agents that speed up biochemical reactions. We have proposed the use of nanocatalysts for the support of pyrolysis gasification and transesterification. Moreover, this step will make extracting the maximum energy from biological sources faster and easier (Abdelhady et al., 2020). A nanomaterial made from metal was used as a catalyst to accelerate the process. Nanocatalysts are becoming increasingly popular for transesterification due to their high specific surface area and improved catalytic activity (Whangchai et al., 2021). This, in turn, results in a higher biodiesel output than solid catalysts. Nanomaterials, including various designs and establishes, have emerged as significant players in industrial catalysis in recent years.

The heat generated during the pyrolysis process led to the decomposition of biomass in the absence of oxygen. In order to produce a catalyst, this step has to be taken (Ajala et al., 2020). This study will concentrate on the catalyst obtained from biomass and combined with nickel and cobalt nanocatalysts to produce biodiesel from waste cooking oil through the transesterification process. Because used cooked waste oil can be easily found in homes and food shops, it is a good choice for biodiesel production. Therefore, it can be used as a precursor for biodiesel manufacturing. This study's primary objective was biodiesel production to make actual use. Therefore, this research focused on the biodiesel-derived nanocatalyst from biomass to produce biodiesel from cooking oil.

2. Materials and methods

2.1 Barley straw biomass and chemical reagents

Barley straw was carried from the agronomy field zone at Maejo University's Faculty of Agriculture in Chiang Mai, Thailand, to the portable solar dryer and reduced in size with a grinding machine. It is approximately 2-3 centimeters long. This study employed all the chemicals purchased in the analytical grade.

2.2 Nanocatalyst preparations

In a muffle furnace, at 400°C without oxygen and a pressure of 1-5 bar, the biomass of barley straw was determined. The procedures were followed by Ali et al. (2020). First, the dry biomass of three different weeds was mixed in equal quantities to make a composite 100g sample of dried mixed weed biomass. Then, the mixture of dried mixed biomass of nanoparticles of nickel and cobalt (0.5g, 0.5g) was added to a flask with 1% weight of barley straw biomass. The flask went in the muffle oven at 400 °C for 2 h.

2.3 Step-by-step process of biodiesel production

The schematic structure and experimental procedure of biodiesel production are demonstrated in Figure 1. For efficient confirmation studies, molar ratios of methanol:oil (6:1, 9:1, and 12:1) with the amount of catalyst (1, 2, and 3% wt), at 2 hours reaction time. The process is following:

i. A nano catalyst concentration of 2.5 % (0.75g) was added to 30 ml of methanol.
ii. It took nearly an hour to thoroughly dissolve all the catalysts using a hot plate stirrer to agitate the solution.
iii. The catalyst and methanol mixture were added to the waste cooking oil, stirring for 2 hours at 60 °C.
iv. When the reaction was done, the esters and glycerol were separated using a separating funnel and a process called sedimentation.
v. This made it possible to separate the biodiesel and glycerol from the mixture.

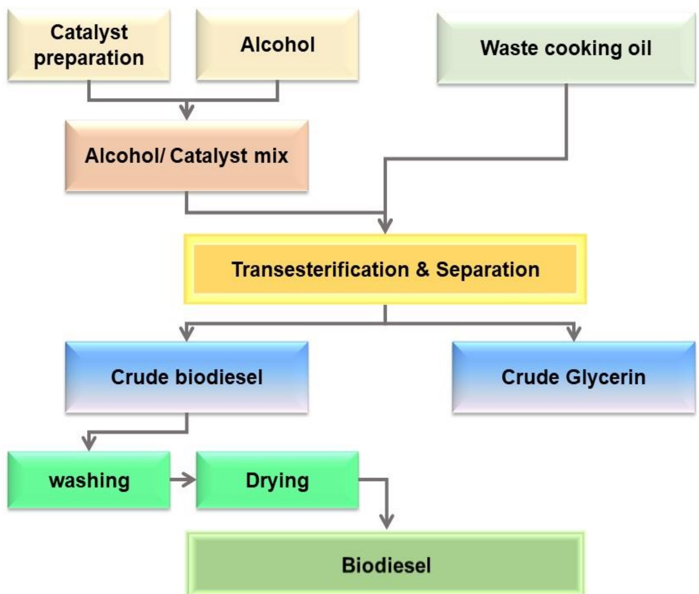

Figure 1 Schematic structure and experimental procedure of biodiesel production

vi. Then, the biodiesel was washed several times with distilled water to eliminate the catalyst and any methanol that had not been used.
vii. This was done until the pH was neutral. Next, distilled water was added to the biodiesel in a beaker and left for 5 minutes.
viii. After that, two layers of water with unreacted methanol and catalyst and a layer of biodiesel formed.
ix. The top layer of water with unreacted methanol and catalyst was removed carefully, and the pH of the biodiesel was recorded.
x. This was done again and again until the pH was neutral.
xi. The clear ester that was made was then dried, and the volume of biodiesel was measured for further analysis.

Biodiesel production procedures and experimental details were adopted by Ramaraj et al. (2016). The data or readings provided are the results of the mean of three replicates. The data were provided using a mean and standard deviation format (SD).

3. Results and discussion

3.1 Biodiesel versus conventional diesel

Biodiesel fuel has many advantages over regular diesel. It is made from animal fats, vegetable oils, or waste cooking oil and has many advantages over petro-diesel (Bohlouli & Mahdavian, 2021). Because of the higher oxygen content in biodiesel, the carbon content of biodiesel is lower than petro-diesel (Ramaraj et al., 2016). As a result, it can reduce the environmental pollution of CO_2 and other pollutants and reduce the emission of polycyclic aromatic hydrocarbons, sulfates, and hydrocarbons (Saengsawang et al., 2020). There are several benefits to biodiesel production from animal fats. These include a decrease in the emissions of aromatic hydrocarbons (by approximately 75-90 %) as well as a reduction of the unburned hydrocarbons (90%). Additionally, the emissions of H_2S and CO, as well as PM and NOx, are significantly reduced. It is more oxygen-rich than regular diesel and has a higher cetane number (CN) than vegetable oil biodiesel. Because animal fat biodiesel is made from animal fat, it has a higher CN than regular diesel (Ramaraj et al., 2016).

Refining biodiesel from animal fat is more expensive than refining biodiesel from vegetable oils (Faruque et al., 2020). Glycerol is a byproduct of transesterification, which can cause a significant reduction in the quality and lifespan of the engine (Whangchai et al., 2021). Biodiesel from WCO is 75% less likely to emit greenhouse gases than diesel fuel. It also has lower CO, CO_2, and sulfur dioxide levels. The CN of biodiesel fuel varies depending on the type of vegetable oil used. It is superior to petro-diesel. Biodiesel made by heterogeneous nanocatalysts produces far less pollution than traditional catalysts. Biodiesel has another advantage: it emits less air pollution than diesel.

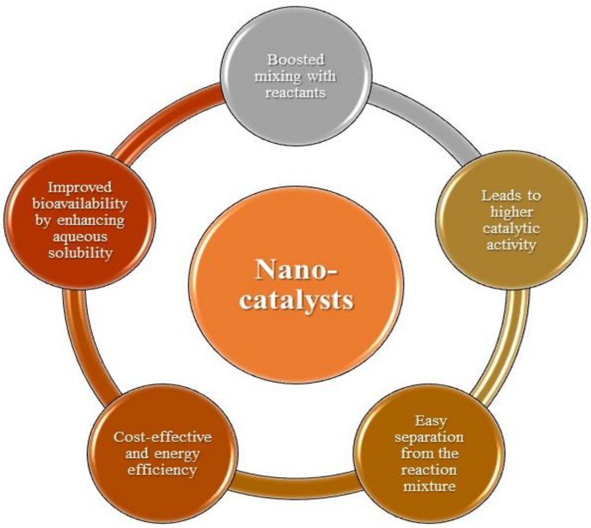

Figure 2 Nano catalysis applications and benefits in the biodiesel production

3.2 The importance of nanocatalysts in biodiesel production

Nanocatalysis is a rapidly growing field of research that studies the use of nanoparticles as catalysts in heterogeneous and homogeneous catalysis for biodiesel production (Zhu et al., 2021). Nanoparticles made of different substances (including metals, semiconductors and oxides) have enhanced and accelerated essential chemical processes in heterogeneous catalysis (Ajala et al., 2020). Nanocatalysis applications and benefits in biodiesel production are presented in Figure 2.

Commercial catalysts are still made by "mixing and shaking" multiple components. There is little or no control over their nanostructures and little understanding of the relationship between synthesis and performance (Abdelhady et al., 2020). Despite the important advances in catalysis research made possible by surface science, this is still true (Zhu et al., 2021). In addition, it is difficult to identify the majority of industrial catalysts because of the complexity of their physicochemical properties at the nanoscale.

To avoid nanoparticles clumping together, they must be stabilized (Faruque et al., 2020). Stabilizers are a key factor in the reactivity of nanoparticles for catalytic applications. Stabilizers protect the nanoparticles from being damaged in catalytic processes without making them ineffective. The balance between the passivation of nanoparticle surfaces and the number of catalytic sites is essential. This can impact the final size and structure of the nanoparticles. The method for creating heterogeneous metal nanocatalysts uses lithographic methods to produce nanostructures on supports and then adsorption of nanoparticles onto them.

3.3 Study on biodiesel production by transesterification reaction from waste cooking oil by using nanocatalyst

To study the optimum factors for biodiesel production by transesterification reaction from used waste cooking oil, i.e., temperature for synthesizing nanocatalyst from barley straw using nickel and cobalt molar ratio of methanol to oil. The amount of catalyst and reaction time can be explained in the methodology part. The effect of methanol on oil and the temperature of the missed biomass derived towards biodiesel production. The molar ratios of methanol to oil were studied at 3:1, 6:1, and 9:1 using catalysts. The reaction time of all ratios was 2 h with the amount of catalyst used was 2%wt. The reaction temperature was controlled at 60 ºC, and the stirring rate was 300 rpm. The results are shown in Table 1.

Table 1 Biodiesel yields from different molar ratios and catalyst concentration

Molar ratios of methanol to oil	Biodiesel yield (%)		
	Nano-catalyst (1%)	Nano-catalyst (2%)	Nano-catalyst (3%)
3:1	84.01±2.35	87.77± 1.46	89.01±1.75
6:1	94.55±2.83	98.92±1.04	95.61±2.11
9:1	92.71±2.33	91.13±1.78	90.02±1.04

Table 1 shows the amount of biodiesel yield from the molar ratio reaction by methanol to oil were 3:1, 6:1 and 9:1 from the 1,2 and 3 % of nanocatalyst concentration at 2 hours reactions. The methanol-to-oil ratios of 3:1, 6:1 and 9:1 accounted for more than 80% of biodiesel production. The highest biodiesel yield of 98.92% was obtained from the reaction at a 6:1 molar ratio of methanol to oil. The methanol-to-oil ratio increased to 9:1, and the biodiesel output decreased. Encinar et al. (2022) stated that the ratio by excessive moles of methanol per oil would make the ability to dissolve the catalyst increase reaction and the biodiesel amount thus decreased.

Furthermore, nanocatalysts have been utilized to make biodiesel, and they are thought to be excellent for making biodiesel from inexpensive feedstocks (Mokhatr and El-Faramawy, 2021). Therefore, nanocatalysts, 6:1 ratio, and 2% catalyst are suitable for further scale-up studies. The economic profitability of transesterification reaction biodiesel production depends on process intensification, alcohol and catalyst amounts and kinds, oil content, residence length, and temperature. Biodiesel is primarily batch-produced. Continuous process mode reduces space, capital, and operating cost and ensures product quality (Ajala et al., 2020).

This processing mode is suitable for quick responsiveness and heat transport. In addition, continuous processing is helping the biodiesel industry overcome batch process restrictions (Faruque et al., 2020). Enhancing energy security, rural development, and a shift to a low-carbon economy are all major contributors to the growth of biodiesel production, which in turn helps mitigate climate change. Nanocatalysts improve biodiesel's long-term viability through various procedures, including substituting heterogeneous (non-basic) catalysts, calcium-based catalysts, and dry-washing purification.

4. Conclusion

Nanocatalysts can be employed in laboratories instead of bulk catalysts due to their slow activation rate and absence of mass transfer resistance. High catalytic efficiency nanocatalysts are more efficient under mild operating conditions for biodiesel production. This results in lower energy consumption. Because they prevent nanoparticle loss and increase their recovery rate during separation, magnetic nanocatalysts are especially promising for biodiesel production from the transesterification of waste cooking oils. This paper examines the production of nanocatalysis biodiesel using waste oils through transesterification processes. Under mild operating conditions, the reaction occurs in the presence of nanocatalysts. The reaction results at the molar ratio of methanol to oil 6:1 using nanocatalyst at 2%wt, reaction time 2 hours, with a maximum and biodiesel yield of 98.92%, was obtained by transesterification. Nanocatalysts with high activity and selectivity for biodiesel generation at the industrial scale need further research into their economic viability.

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