



Nanoferrites heterogeneous catalysts for biodiesel production from soybean and canola oil: a review

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Abstract

Fossil fuel depletion and pollution are calling for alternative, renewable energies such as biofuels. Actual challenges include the design of efficient processes and catalysts to convert various feedstocks into biofuels. Here, we review nanoferrites heterogeneous catalysts to produce biodiesel from soybean and canola oil. For that, transesterification is the main synthesis route and offers simplicity, cost-effectiveness, better process control, and high conversion yield. Catalysis with nanoferrites and composites allow to obtain yields higher than 95% conversion with less than 5.0 wt.% of catalyst loading at 80 °C in 1–2 h. More than 90% conversion yields can be achieved with a moderate alcohol/oil molar ratio, i.e., between 12:1 to 16:1. Catalyst recovery is easy due to the magnetic properties of nanoferrite, which can be effectively reused up to 4 times with less than 10% loss of catalytic efficiency.

Keywords Renewable energy · Biodiesel · Transesterification · Catalysis · Heterogeneous catalysts · Nanoferrites

Introduction

The energy required to run any conventional powerplant generally comes from converting the calorific value of a fossil-based fuel into a propulsive force. Petrol, diesel, compressed natural gas, and high-grade kerosene are fundamental fossil-based fuels, being extensively used in automobiles, trains, ships, and aircraft powerplants (Abas et al. 2015; Martins et al. 2019). As per the monthly oil market report (MOMR) of April 2021, published by the Organization of the Petroleum Exporting Countries (OPEC), the global oil demand in 2021 is expected to rise to an average of 96.5 million barrels per day (mb/d) in contrast to an average of 90.5 mb/d in 2020. One key factor in this projected upsurge in the global oil demand is the unavoidable industrial and

anthropogenic rebound of the globally imposed COVID-19 lockdown measures in the year 2020. The report concluded that the average global consumption of gasoline and diesel over the first quarter of the year 2021 was around 24.0 and 26.3 mb/d, which is forecasted to increase to 25.6 mb/d and 26.6 mb/d in the 2nd quarter of the year 2021, respectively. Researchers have predicted that by the year 2030, world oil consumption will increase to 118 mb/d and, given this rate, the global crude oil reserves will deplete by the year 2060 (OPEC 2021).

The threat of accelerated climate change due to CO₂ emissions upon fossil-based fuel combustion for energy consumption is also an area of global concern (Osman et al. 2020). These fossil-based fuels tend to produce harmful combustion products, i.e., CO, CO₂, NO_x, SO_x, and carbon particulates, due to their chemical composition (Perera 2018; Kumar et al. 2020). The latest reports stated that in December 2020, the global CO₂ emissions had increased by 60 million tonnes in contrast to reported global emissions in December 2019. Over the period from the year 2014–2019, an annual increase of 1.3% had been observed in the energy-related global CO₂ emissions (Energy & Carbon Summary 2021; GEP 2021). This steady increase had been achieved due to the collective efforts of the 191 members of the United Nations Framework Convention on Climate Change (UNFCCC), collaborating under the aegis of the

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international treaty on climate change, known as the Paris Agreement. The Paris Agreement is dedicated to decreasing the global risks of climate change through making incessant efforts towards its long-term agenda to limit the rise in the global average temperature by 1.5 °C (UN 2015). However, the constraints and limitations imposed on various anthropogenic activities due to the COVID-19 global pandemic led to a 7% decrease in global emissions (Le Quéré et al. 2020). Along with harmful combustion emissions, the extraction and refining procedures to convert the crude oil into appropriate grade fuels also negatively affect the environment (Lazarus and van Asselt 2018; Gielen et al. 2019). The increased demand and limited supply of exhaustible reserves tend to increase the cost of these fossil-based fuels (Shafiee and Topal 2010). West Texas Intermediate (WTI) reported that the average monthly crude oil price has increased to \$62.33 per barrel in March 2021 compared to \$29.21 per barrel in March 2020 (USEIA 2021a).

The limited reserves of fossil-based fuels and their inherent environment-polluting tendencies upon combustion have enticed all stakeholders' attention towards exploring and utilizing renewable, alternative, and less environmentally detrimental substitutes (Owusu and Asumadu-Sarkodie 2016; Jain 2019). The continuous growth in the human population and the industrial sector has imposed ever-increasing demands for energy, necessitating augmented utilization of fossil-based fuels (Johnsson et al. 2018). In January 2021, the Organisation for Economic Co-operation and Development (OECD) regions of America, Europe, and Asia indigenously produced a total of ~ 105 million metric tonnes of crude oil, natural gas liquids, and feedstocks (USIEA 2021). It has become imperative and almost unavoidable to explore cleaner and renewable energy resources to meet these imposed requirements. Continuous efforts are being made to explore various suitable eco-friendly candidates that can either partially substitute or completely replace the conventional fossil-based fuels for power generation in existing powerplants (Abbasi et al. 2011; Lelieveld et al. 2019; Shokrani and Haghghi 2020). As a result, a gradual transition towards using clean energy driven by various policies and innovations in renewable energy production and consumption can be seen. The global use of renewable energy in all sectors has increased by 1.5% in the first quarter of 2021 relative to 2020. Renewable energy only comprised just around 8.6% of the global energy mix in 2010, which increased to about 23% by the year 2020 (IRENA 2020).

Biodiesel has turned up as one of the prevailing alternative and renewable fuels by facilitating decreased pollution emissions and ease of production and use (Huang et al. 2012). Biodiesel offers significant advantages over traditional petrodiesel, particularly in renewability, non-toxicity, biodegradability, superior lubricating characteristics, cleaner combustion, and lower emission profiles (Atabani et al.

2012). Biodiesel has the potential to deliver comparable performance while substantially reducing the demand and reliance of the energy and transportation sector on various petroleum-derived fuels (Chaker Ncibi and Sillanpaa 2014). Figure 1 depicts how the synthesis and application of biodiesel for energy generation in different techno-economic sectors of society can lead to enhanced eco-friendliness, renewability, and sustainability. From environmental consideration, biodiesel's production cycle and application lead to lesser greenhouse gas emissions than petrodiesel (Zentou et al. 2019; Srivastava et al. 2020). On the socio-economic front, biodiesel's application enhances employment by providing income generation opportunities and improves the prospects of rural development by promoting farming of the feedstocks (Das 2020).

The catalyst plays a crucial role in the conventional synthesis process of biodiesel. Various catalysts have been used and investigated for biodiesel synthesis, and every catalyst offers specific advantages and limitations. Nanoferrite is a category of ceramic materials that have continuously gained attention as heterogeneous catalysts for biodiesel production. The peculiar physical, chemical, structural, electrical, and mechanical characteristics of nanoferrites exhibit remarkable advantages over traditional heterogeneous catalysts (Thakur et al. 2020). We aim to provide an overview of the transesterification route of biodiesel synthesis and the role and characteristics of catalysts in the synthesis reaction. Although a growing field of research, only a few studies have been conducted about using nanoferrites as heterogeneous catalysts to synthesize biodiesel. We have reviewed the research, essentially reported in the last ten years, i.e.,

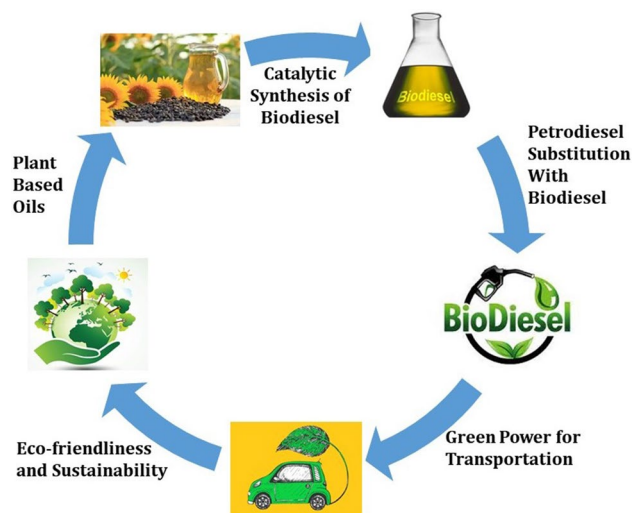


Fig. 1 Role of biodiesel in improving renewability and sustainability of the energy generation processes. The boost in the application of biodiesel tends to decrease the detrimental consequences on the local and global environment leading to enhanced eco-friendliness

between the years 2010 and 2020, and have reported the recent advances and developments about the application of nanoferrites as heterogeneous catalysts for the synthesis of biodiesel using soybean and canola oil.

Biodiesel as a clean fuel

Categories of biofuels

All the liquid- or solid-phase renewable alternative fuels are collectively termed biofuels (Ong et al. 2019). Depending on the feedstock, biofuels can be classified into various categories, as shown in Fig. 2 (Alalwan et al. 2019). Though biofuels’ structure is similar in all three generations, they differ entirely in their feedstock. The production of the first-generation biofuels generally employs hydrolysis and fermentation of starch, availed from edible feedstocks (Hajilary et al. 2019). The dependency of this generation of biodiesel on edible feedstocks often raises a debate between food versus fuel requirements (Saladini et al. 2016). The

second-generation biofuels are generally called advanced biofuels as they do not compete with the food supply and thus are sustainable. The second-generation biofuels are produced as the feedstocks undergo biochemical or thermochemical conversion processes such as gasification, pyrolysis, or torrefaction. The feedstock for second-generation biofuels is generally unsuitable for human consumptions, can grow on marginal lands, and require minimum to negligible amounts of fertilizers. They do not pose any threats to land availability, water availability, food sources, wildlife, marine life, and the ecosystem (Bhuiya et al. 2016; Bhatia et al. 2017).

The inherent requirements of farming land, irrigation, and fertilizers impose certain constraints on harvesting large quantities of feedstocks to produce first- or second-generation biofuels. These problems are mitigated by third-generation biofuels that rely on algal species, providing unmatched amount and diversity to produce biofuels (Patle et al. 2021). It is acknowledged that algae can thrive even under adverse growth conditions and provide various products (Rashid et al. 2014; Mofijur et al. 2019). Figure 3

Fig. 2 Categories of biofuels. The first-generation biofuels pose a threat to food availability due to their edible feedstocks, while the production of second- and third-generation biofuels is more preferred due to their inedible feedstocks

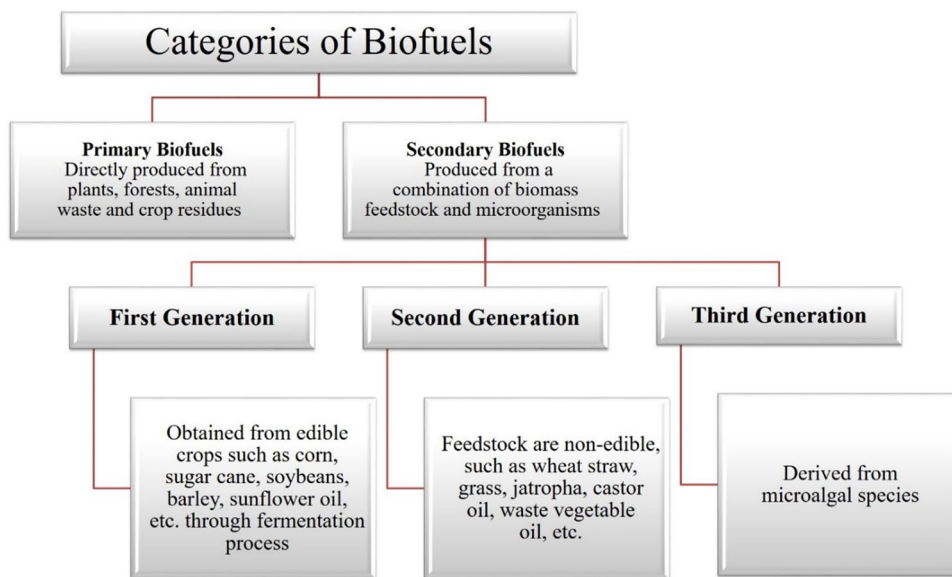
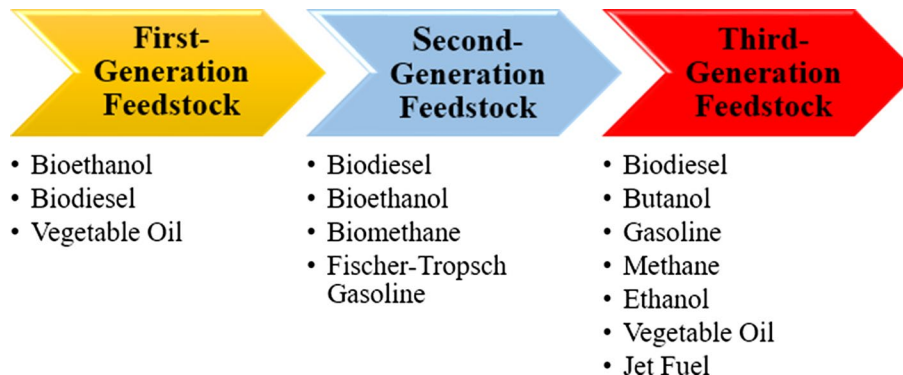


Fig. 3 Various biofuel derivatives from different feedstocks. More number of biofuel variants can be obtained from third-generation feedstocks. The simplicity of harvesting algae and extracting algal oils makes biofuels of the third generation compared to the two former generations



represents the different products derived from first-, second-, and third-generation feedstocks (Rashid et al. 2014; Bhuiya et al. 2016; Saladini et al. 2016; Bhatia et al. 2017; Mofijur et al. 2019).

As per the Global Bioenergy Statistics 2020 report, globally, the domestic supply of biomass has increased from 42.5 exajoules (EJ) in the year 2000 to around 55.6 EJ in 2018. During this period, liquid biofuels showed the fastest growth of ~13% compared to other variants of biofuels. In the year 2018, Asia and Africa together contributed around 35.6 EJ of domestic biomass supply. In the year 2000, around 17.3 billion litres of biofuel were being produced, which increased to around 160 billion litres by 2018. Among the continents, America alone contributes to around 87% of bioethanol production (World Bioenergy Association 2020). A steep rise in the production and application of bioenergy has been observed during the last two decades. The availability of feedstocks and the cost-effectiveness of the biofuel production process is one of the critical factors that drive the interest in any given generation of biofuels. We reiterate that even though the first-generation feedstocks facilitate an efficient biofuel production process, the second-generation biofuels are considered comparatively greener owing to their sustainability characteristics.

Evolution of biodiesel

In the nineteenth century, the famous German inventor and mechanical engineer Dr. Rudolf Diesel, the inventor of the diesel engine, instigated the interest in studying various vegetable oils as an alternative to fossil-based fuels (Bušić et al. 2018). The then French government researchers and Dr. Diesel conducted experiments and concluded that vegetable oils *in natura* pose several operating issues (Zahan and Kano 2018). They observed that vegetable oil's direct injection led to improper atomization due to its high viscosity and low volatility. This inadequate atomization further led to incomplete combustion of the oil and subsequent deposition of carbon content on the engine's valves and nozzles. These operation-related problems associated with the use of vegetable oils in diesel engines collectively lowered down the engine's output efficiency along with toxic and hazardous emissions (Ogunkunle and Ahmed 2019). Belgium inventor G. Chavanne of the University of Brussels addressed the issues mentioned above (Balasubramanian and Steward 2019). His efforts were directed towards refined vegetable oils to obtain thinner products of comparable specific gravity as fossil-based diesel or petrodiesel. He laid the foundation of the next major milestone in the evolution of biodiesel when in the year 1937, he received a patent on his article titled, *Procedure for the transformation of vegetable oils for their uses as fuels* (Piloto-Rodríguez et al. 2014). In his article, he reported converting palm oil into ethyl ester through a

chemical process known as transesterification. As a fruitful practical trial of his research and efforts, a palm oil ethyl ester-fuelled passenger bus plied between the cities of Brussels and Louvain in the year 1938 (Satya et al. 2019).

In 2018, biodiesel contributed around 26% of the globally produced 160 billion litres of biofuels. The average per-day production of biodiesel and hydrotreated vegetable oil (HVO) has increased from around 353,000 barrels in 2010 to 792,000 barrels in 2020, which is forecasted to increase to around 1,116,000 barrels by 2025. In 2009, biodiesel's share in total biofuel consumption was around 23%, which has increased to 37% by the year 2019 (USEIA 2021b). In the European Union (EU), Germany has been leading the production of first-generation biofuels since 2004 (ETIP Bioenergy 2020). We can safely state that the growth of the biofuel industry has indeed come a long way since the first passenger vehicle operated on biodiesel. By the end of the year 2021, the global biofuel market is expected to grow to around USD 44.5 billion. The global transport biofuel production has expanded around 6% year-on-year to reach ~160 billion litres in 2019. However, this production needs to be tripled by 2030 to align with the Sustainable Development Scenario (SDS) (UNDESA 2019).

The biodiesel's chemical composition generally contains almost negligible sulphur content, no aromatics, and a substantial amount of oxygen by weight. These compositions reduce CO, NO_x, SO_x, hydrocarbon, and particulate matter via exhaust gases (Balajii and Niju 2019). Accordingly, the American Society of Testing and Materials (ASTM), via standard ASTM D6751-20, and the European Committee for Standardization via standard EN 14,214 describe test methods and standard specifications for 100% biodiesel (B100) fuel stock (Berrios et al. 2011; Hassan and Kalam 2013; Singh et al. 2018). Biodiesel exhibits a comparatively higher cetane number than petrodiesel in terms of performance, delivering shorter ignition delay times and efficient combustion (Atabani et al. 2012; Hayes et al. 2015). Biodiesel delivers significant advantages due to its ability to be used independently or in-blend with petrodiesel while demanding almost no modification in conventional diesel engines (Imdadul et al. 2017; Mahmudul et al. 2017; Srithar et al. 2017). The B20 is the most common biodiesel blend, which may comprise 6% to 20% of biodiesel blended with petrodiesel. However, the B5 blend, which comprises 5% biodiesel blended with 95% petrodiesel, has also been used in various fleet vehicles (USEIA 2021b).

Different types of biodiesel have emerged as competitors to petrodiesel in many technical characteristics. One of the critical limitations of any renewable and greener substitute is to keep the requirement of modifications in the components and structure of the existing powerplant to a minimum while delivering adequate performance and reduced environmental threats. The quality of biodiesel also plays a decisive

role in its utilization as it governs the engine's performance and overall lifespan. Therefore, it is crucial to monitor and maintain biodiesel's quality to ensure optimum output and efficiency of the engine. Diesel has an energy density of around 38.6 MJ/l, whereas biodiesel exhibits an average energy density of 34.5 MJ/l. These comparable energy densities of diesel and biodiesel allow for partial substitution of diesel with biodiesel without any significant modifications in existing engines.

Limitations of biodiesel

Biodiesel is rapidly emerging as the preferable alternative for fossil-based fuels. The production and use of biodiesel offer significant economic and technological advantages and disadvantages due to their inherent characteristics. Although biodiesel has the potential to minimize the release of greenhouse gases, the notion of completely substituting petrodiesel with biodiesel is practically challenging. One major challenge is the tendency of the cellulosic feedstock to compete with the food supply chain and resources, in one way or another. The escalation in feedstock farming may lead to food, land, water, fertilizer, and workforce shortage. Depending on the feedstock, i.e., edible, used edible, inedible, or waste products, the biodiesel cost may become higher than that of the petrodiesel. Significant differences in the feedstock and biodiesel synthesis processes may lead to biodiesel production with varying physical and chemical properties. Such variability in the composition and performance of biodiesel may lead to complications in systems' interchangeability.

The comparatively lower shelf life of biodiesel is also a limiting factor since it tends to increase the overall cost of storage, transport, and handling. Biodiesel is also known to perform inadequately in low-temperature conditions, leading to reduced engine performance. These constraints also give rise to the phenomenon of regional suitability of biodiesel. Another area of concern that arises due to this local suitability, along with excessive farming of biodiesel feedstock, is the practice of monoculture. Monoculture results in continuous extraction of specific nutrients and minerals from the soil because of repeated farming of the same crop over a prolonged period. This practice essentially reduces the fertility and versatility of the farming land, making it inadequate to sow different crops. We affirm that the limitations and constraints mentioned above may reasonably be evaded by implementing carefully designed policies and protocols about biodiesel feedstocks' farming at an industrial scale. One such step towards these effective policies is the National Policy on Biofuels, formulated and implemented by India in May 2018, aiming to achieve a 20% blending of fossil-based fuels with biofuels by 2030.

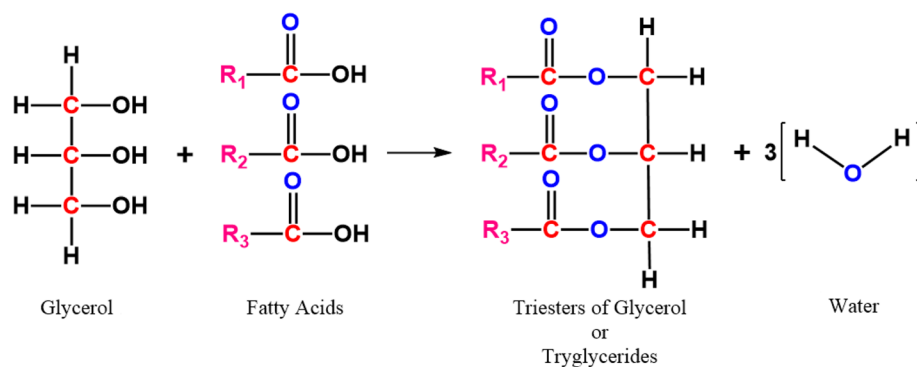
Biodiesel synthesis route—transesterification

The primary raw material utilized for biodiesel production is an animal or plant-based lipid, making biodiesel of renewable nature as it does not depend on exhaustible resources (Lei et al. 2011). Biodiesel can be obtained through various chemical processes such as transesterification, esterification, cracking, hydroesterification, pyrolysis, and esterification followed by transesterification (Sánchez Faba et al. 2019). Among these, transesterification and esterification are the most straightforward and preferred processes to produce biodiesel. These processes are carried out by facilitating a reaction between any feedstock-derived oil and alcohol in the presence of a suitable catalyst (Maddikeri et al. 2012).

Triglycerides are produced when three fatty acids combine with glycerol and are chiefly found in humans and animals as body fat and as vegetable oils in plants. (Asakuma et al. 2009; Mishra and Goswami 2018). Triglycerides are primarily classified as saturated and unsaturated types. In saturated triglycerides, all the vacant places in the chemical structure are occupied by hydrogen atoms bonded with carbon atoms. Saturated triglycerides are generally called fat, are solid at standard pressure and temperature and exhibit a higher melting point. In unsaturated triglycerides, generally called oil, fewer vacant places are available for the hydrogen atoms to bond with carbon atoms due to the presence of double bonds in the chemical structure. At standard pressure and temperature conditions, oils are generally liquid and exhibit a lower melting point than fats. Alcohols consist of a hydroxyl (–OH) group, while organic acids consist of a carboxyl (–COOH or –CO₂H) group. One –COOH or –CO₂H group is present with each fatty acid, whereas three –OH groups are available in the glycerol molecule. Esters are formed upon combining alcohols and organic acids (Oliveira et al. 2010; Hayyan et al. 2014). A typical synthesis reaction for the production of triglyceride is illustrated in Fig. 4.

The transesterification process is the conversion of one ester into another in the presence of any given alcohol. The transesterification process, also known as alcoholysis, is the widely used route for reducing the viscosity of the triglycerides and produce fatty acid esters (FAEs). The rate of the transesterification reaction can be accelerated by including either an acid or a base catalyst. The reaction between triglycerides and alcohol leads to the production of esters and glycerol (Kumar and Ali 2013). Therefore, the biodiesel produced through the transesterification or esterification route is aptly called fatty acid mono-alkyl ester obtained from edible or inedible renewable feedstock. Short-chain alcohols, i.e., methanol or ethanol,

Fig. 4 Synthesis reaction and structure of triglycerides. Three parts of fatty acids combine with one part of glycerol to produce one part of triglycerides and three parts of water



are generally preferred for the transesterification process. Methanol is a polar molecule, which exhibits high reactivity. Subsequently, the reaction of triglycerides with methanol and ethanol tends to produce fatty acid methyl ester (FAME) or fatty acid ethyl ester (FAEE), respectively, along with glycerol (Da Silva et al. 2015). The selection of methanol or ethanol as the preferred alcohol is due to their comparatively lower prices than other high-boiling-point alcohols. The steric hindrance phenomenon is also avoided by using short-chain methyl and ethyl alcohol, and improved efficiency of the transesterification process is achieved (Mendow and Querini 2013; Da Silva et al. 2015). The chosen feedstock for biodiesel production should have low levels of free fatty acids (FFA) to minimize losses in ester's conversion and avoid saponification during the transesterification process. Therefore, the search for potential raw materials that can provide large quantities of fatty materials is usually limited by their FFA contents (Bouaid et al. 2016). Figure 5 illustrates the reaction for synthesizing methyl ester through the transesterification process in the presence of a suitable catalyst.

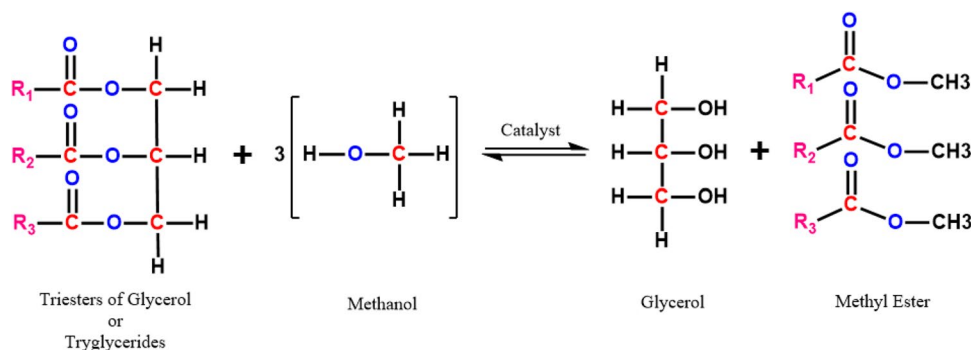
We recommend that using esterification and transesterification processes offer significant advantages compared to other synthesis processes. The transesterification process is an eco-friendly yet straightforward process and can be carried out under mild operating conditions. The alcohols used in the process are effective, inexpensive, and readily available. The transesterification process is a versatile process that

offers shorter reaction times and crucial flexibility in selecting the raw ingredients and catalysts for biodiesel synthesis. The transesterification process can be employed to produce biodiesel in both batch mode and continuous production. The latter method requires comparatively lesser labour costs, capital, and downtime time than the former way of biodiesel production.

Kinetic modelling of transesterification reaction

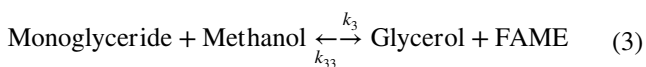
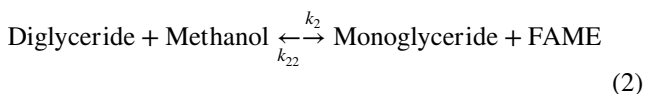
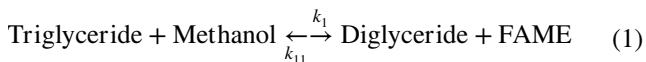
The rate of a chemical reaction can be assessed by studying the kinetics of the reaction. The kinetic model provides valuable information about the reaction's course at each step of a multi-step reaction (González-Brambila et al. 2014). Consequently, various order kinetic models, such as zero-order, first-order, second-order, pseudo-first-order, and pseudo-second-order, are available to evaluate the dependency of the transesterification reaction on reaction rate and other components of the reaction process. Transesterification kinetics is a tool used by researchers to establish the mathematical relationship between the reaction temperature and time under optimized process conditions (Singh and Fernando 2007). A reversible transesterification reaction may follow various order reactions when the reaction yield is examined as a function of reaction time, depending upon the reaction's different independent variables. A model with

Fig. 5 Synthesis reaction of methyl ester. One part of triglycerides is reacted with three parts of methanol to produce one part of glycerol and one part of methyl ester. Methanol is the preferred alcohol and produces methyl esters. Ethyl ester is produced if ethanol is used in the synthesis procedure



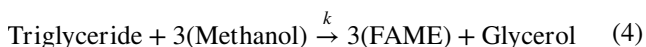
varying order of reaction and the maximum value of the regression coefficient R^2 would be considered the best fit for a given transesterification reaction with specific reaction parameters (He et al. 2007).

The overall transesterification process can be described as the three consecutive reversible processes where mono-glycerides and diglycerides are formed during the intermediate steps. Equations 1, 2, and 3 represent the reversible processes involved in converting triglycerides into fatty acid methyl esters (FAME) and glycerol in the presence of methanol as an example (Singh and Fernando 2007).



where k_1 , k_2 , and k_3 are the rate constants for intermediate forward reactions while k_{11} , k_{22} , and k_{33} are the rate constants for reverse intermediate reactions.

We recommend that alcohol must be added in excess to obtain a high yield from the transesterification process. Due to the high alcohol to oil molar ratio, intermediate reverse reactions can be ignored, while the quantity of methanol available in the reaction can be assumed invariant. Thus, the overall transesterification process is considered a forward reaction of first order and is represented as Eq. 4 (Gurunathan and Ravi 2015a).



where k is the reaction rate constant for the transesterification process that can be obtained for the available triglyceride content (TGC) in the reaction at a given instant of time. Mathematically, the first-order kinetic equation relates to the triglyceride content (TGC) and rate constant of the reaction and can be expressed by Eq. 5 (Gurunathan and Ravi 2015b; Hindryawati and Maniam 2015).

$$-\frac{d[\text{TGC}]}{dt} = k[\text{TGC}] \quad (5)$$

Equation 5 can be rearranged to formulate Eq. 6.

$$-\frac{d[\text{TGC}]}{[\text{TGC}]} = kdt \quad (6)$$

A linear curve can be obtained by plotting $\ln [\text{TGC}]$ against $\ln \frac{d[\text{TGC}]}{dt}$ at different time intervals for different temperatures. The fitted linear curve's intercept and slope provide the value of the reaction rate constant, k (Suganya

et al. 2013). The zero-order transesterification reaction can be given by Eq. 7.

$$\frac{d[\text{TGC}]}{dt} = k[\text{TGC}] \frac{dx}{dt} \quad (7)$$

where x is the fraction of TGC in the reaction mixture.

The activation energy required for carrying out the transesterification process generally depends upon the reaction parameters and, subsequently, on the reaction rate constant, k . The Arrhenius equation is used to calculate the activation energy and is expressed as Eq. 8.

$$k = Ae^{\frac{-Ea}{RT}} \quad (8)$$

where A is the Arrhenius constant, Ea is the activation energy (Jmol^{-1}), R is the universal gas constant ($\text{Jmol}^{-1} \text{K}^{-1}$), and T is the absolute temperature (K) (Hindryawati and Maniam 2015; Baskar et al. 2017).

Taking log on both sides of Eq. 8 gives Eq. 9 and is expressed as,

$$\ln(k) = \frac{-Ea}{R} \left(\frac{1}{T} \right) + C \quad (9)$$

The activation energy can be calculated using the slope and intercept of the fitted linear curve obtained by plotting $\ln(k)$ against $(1/T)$ (Firdaus et al. 2016; Baskar et al. 2017).

We conclude that the transesterification yield increases with increasing reaction temperature and time, and the reaction rate constant tends to increase with increasing reaction temperature. The reverse reactions are observed to follow the second-order kinetic models. However, in most cases, pseudo-first-order or pseudo-second-order reactions are a comparatively better fit for the forward reactions.

Characteristics of traditional catalysts

Several crucial variables, such as type of alcohol, oil to alcohol ratio, reaction temperature, reaction time, quality of reactants, and type and quantity of catalysts in the reaction, are involved in biodiesel synthesis (Chozhavendhan et al. 2020). One of these critical variables that govern the transesterification process's overall efficacy is the catalyst, as a suitable catalyst tends to accelerate the reaction rate (Jamil et al. 2018; Chozhavendhan et al. 2020). It reduces excess alcohol use by facilitating an equilibrium adjustment towards glycerol and fatty acid mono-alkyl ester formation. An efficient catalyst decreases the energy necessary for the reaction to occur and subsequently reduces the reaction duration. A suitable catalyst in the reaction having high activity and stability leads to improved reaction yields (Thangaraj et al. 2019; Rizwanul Fattah et al. 2020). Homogeneous as well as heterogeneous acid and base catalysts have been used in the

transesterification process to synthesize biodiesel (Borges and Díaz 2012; Jeon et al. 2019). Each type of catalyst offers specific advantages and intrinsic limitations for its efficient use in biodiesel synthesis. Figure 6 represents the various classes in which available catalysts are categorized (Lam et al. 2010; Borges and Díaz 2012).

Homogeneous catalysts

Homogeneous catalysts having the same phase as reactants are widely used to produce biodiesel. Sulphuric acid, hydrochloric acid, sodium methoxide, sodium hydroxide, potassium methoxide, and potassium hydroxide are among the widely used homogeneous acid and base catalysts (Bohlouli and Mahdavian 2019). The use of homogeneous base catalysts facilitates high yields of FAMES and FAEEs, within about an hour of reaction time and mild reaction conditions (Vyas et al. 2010). In contrast, homogeneous acid catalysts take longer for the ester conversion process and require comparatively higher reaction pressure and temperature conditions (Marchetti et al. 2011). Despite faster reaction times and highly efficient conversion yields provided by the homogeneous catalysts, their similar phase as that of the reactants poses a limiting characteristic resulting in their restricted application in biodiesel production (Marchetti et al. 2011; Thanh et al. 2012). Homogeneous catalysts are prone to dissolve in the mono-alkyl ester and glycerol mixture. It becomes too time-consuming and cost-ineffective to separate the homogeneous catalyst and purify the product after the transesterification process. The separation and purification process often produce large quantities of chemical wastewater, leading to pollution and environmental contamination (OA et al. 2019). Saponification and emulsification

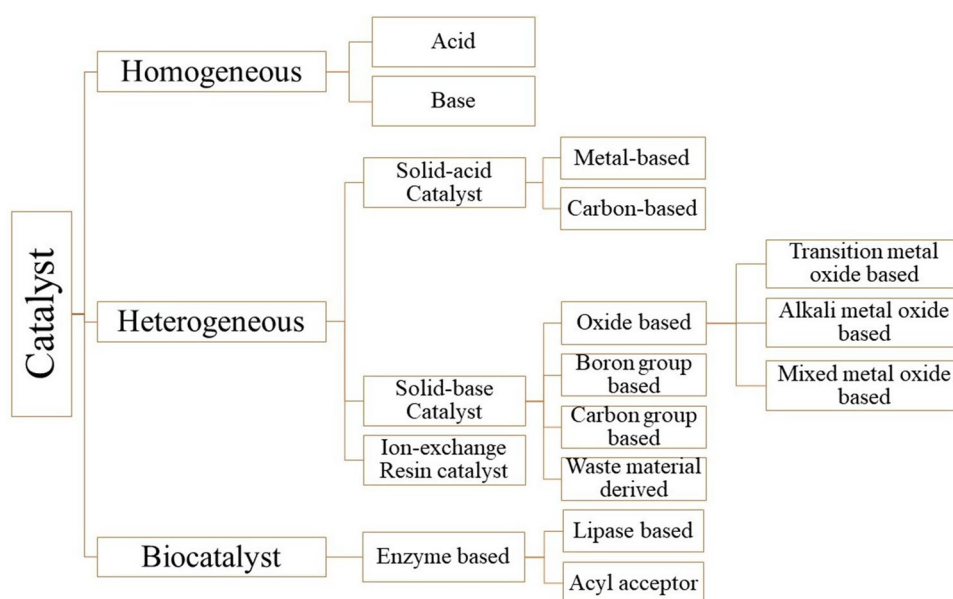
during the transesterification process tend to increase the production cost and reaction time and reduce the overall yield (Fadhil et al. 2018; Krishnamoorthi et al. 2018; OA et al. 2019). The significant drawbacks mentioned above have limited the scope for extended development and commercialization of biodiesel synthesized using homogeneous catalysts.

We conclude that the notable inevitable disadvantages of using homogeneous catalysts are the difficulty in separation and reusability of the catalyst. The problem of equipment corrosion is also a significant challenge and limiting factor in biodiesel's industrial-scale synthesis by using homogeneous acid catalysts. The necessity of specified chemicals to neutralize the catalysts after the reaction tends to present difficulties in reclaiming and reusing the homogeneous catalysts. The loss of catalyst and complexities in synthesized biodiesel separation makes homogeneous catalysts a comparatively less cost-effective method to produce biodiesel.

Heterogeneous catalysts

The inherent difficulties, limitations, and challenges in applying homogeneous catalysts can be evaded using heterogeneous acid and base catalysts (Farooq et al. 2013). The phase of the heterogeneous catalysts is different from the phase of reactants and products. This favourable physical property facilitates easier catalyst separation from the reaction mixture through conventional separation techniques such as centrifugation, filtration, and sedimentation (Diamantopoulos 2015). The comparatively simpler and faster separation of the catalyst from the reactants reduces post-reaction treatment time and cost of the biodiesel synthesis process (Wilson and Lee 2012). The heterogeneous phase

Fig. 6 Classification of catalysts for biodiesel synthesis. Homogeneous catalysts are highly reactive, but their use poses complications in the biodiesel separation process. Heterogeneous catalysts mitigate these difficulties associated with the removal of the catalysts from the mixture. This advantage allows for the development of more variants of heterogeneous catalysts can be developed



of the catalysts considerably reduces the environmental impacts of the process as the quantity of chemical wastewater produced is substantially decreased (Dhawane et al. 2018; Faruque et al. 2020).

Heterogeneous catalysts offer a comparatively environment-friendly and inexpensive alternative for producing high-grade biodiesel with high yield in lesser reaction times (Lee and Saka 2010). Additionally, heterogeneous catalysts allow high molecular weight alcohols to be used and often prove efficient in reactions where homogeneous catalysts are generally inactive. The solid-base heterogeneous catalysts have been extensively studied by researchers as their catalytic activity is greater than that of the solid-acid heterogeneous catalysts, and they offer higher conversion rates at lower reaction temperatures (Hossain et al. 2019; Vasić et al. 2020). A suitable heterogeneous catalyst must be highly stable, mesoporous, inexpensive, and benign (Changmai et al. 2020). It must have strong active sites, multi-functionality, and a long life cycle to replace a homogeneous catalyst successfully. A heterogeneous catalyst's multi-functionality makes it highly competitive and versatile for its use in the relevant areas (Chouhan and Sarma 2011). Heterogeneous catalysts are receiving attention from researchers due to their tendency to consume minimum energy for separation. Easily separable heterogeneous catalysts essentially bring down the cost of industrial-scale biodiesel synthesis processes. Solid catalysts offer the advantage of being incorporated into a packed bed continuous flow reactor, allowing biodiesel production through a continuous system (Colombo et al. 2017). Despite their inherent advantages, most of the available heterogeneous catalysts lack high catalytic activity and stability than homogeneous catalysts (Chouhan and Sarma 2011; Colombo et al. 2017; Changmai et al. 2020).

In recent times, more and more heterogeneous catalysts are replacing homogeneous catalysts. Easy retrieval of the heterogeneous catalyst after separation allows for reusability and reduces the complete synthesis process steps. The efficient recovery of the heterogeneous catalysts from the substrate mixture enhances the cost-effectiveness of the biodiesel synthesis process. However, the inherent shortcomings of heterogeneous catalysts have triggered and motivated extensive and targeted research in developing and using novel heterogeneous catalysts, which can essentially be promising candidates for their use in the transesterification process.

Nanoferrites as catalysts

In recent years, the evolution of nanotechnology has opened up new frontiers to discover and develop suitable heterogeneous nanocatalysts for biodiesel synthesis (Singh 2017; Sekoai et al. 2019). By 2020, the global nanomaterials

market size had reached USD 9.58 billion and is expected to reach USD 22.9 billion by 2027. However, the all-over nanotechnology's market value is expected to reach USD 125 billion by 2025 compared to USD 75 billion in 2020. According to the reports, the production of nanoparticles has increased from 1000 tons in 2011 to around 58,000 tons by 2020 (USFDA 2020). By the end of the year 2020, almost 9000 types of nanomaterials had already been developed by around 2500 companies active in nanoparticle production and application. This growth in the domain of nanotechnology has led to the possibility of exploring nanoparticles for catalytic applications. The nanoscale heterogeneous catalysts offer all the advantages of conventional heterogeneous catalysts accompanied by high surface area and large area/volume ratio, making them more attractive candidates for the transesterification reaction (Thakur et al. 2015; Pandya et al. 2019; Sekoai et al. 2019). The available higher surface area of such catalysts allows for increased contact between the substrate and the catalyst (Bharti et al. 2020). A high chemical reactivity can be obtained because of higher catalytic active surfaces than conventional catalysts of micro- or milli-scale crystals (Prabu 2018).

Nanoferrites are ceramic powders exhibiting strong ferrimagnetic properties owing to iron oxides being their core component (Rana et al. 2015). The ferrites are classified based on their crystalline structure; (a) hexagonal ($MFe_{12}O_{19}$), (b) garnet ($M_3Fe_5O_{12}$), and (c) spinel (MFe_2O_4), where M generally represents one or more bivalent transition metals (Mn, Fe, Co, Ni, Cu, and Zn) (Bharti et al. 2020; Punia et al. 2020). A nanoscale catalyst with magnetic properties facilitates easier separation and recovery by applying an external magnetic field (Gardy et al. 2019; Thakur et al. 2020). This characteristic minimizes catalyst mass loss and increases the catalyst's reusability compared to conventional separation techniques (Thakur et al. 2012). Nanoferrites deliver remarkable multifunctional properties, such as small crystal size, magnetism, biocompatibility, low toxicity, high reactivity, and high chemical stability (Liu et al. 2016).

Nanoferrites are highly dispersible in the solvents, providing ready availability of active catalytic sites for the surrounding reactants (Liu et al. 2016; Sekoai et al. 2019). At least one of the dimensions of such catalytically active nanoferrites must be in the range of 1–100 nm. Despite being heterogeneous in nature, the nanoscale dimensions of nanoferrites often mimic homogeneous catalysts' interaction characteristics (Erdem et al. 2018). Spinel-type nanoferrites exhibit high cationic mobility, making such nanoferrites more attractive to researchers (Thakur et al. 2012). The catalytic activity of nanoferrites is sometimes higher than that of a few conventional acid catalysts because of the strong ionic interactions and magnetic attraction between the particles. These characteristics lead to the higher stability of the nanoferrites. Often, the existence of strong magnetic

dipole–dipole attractions between the nanoferrite particles leads to aggregation, posing a substantial limitation to their use as catalysts (Rana et al. 2015; Liu et al. 2016). Researchers have been developing and investigating different types of nanoferrites for their application as heterogeneous catalysts facilitating a high catalyst recovery rate (Srivastava et al. 2017; Gardy et al. 2018).

Nanoferrites belong to a class of widely explored nanoparticles. Based on the various physical and chemical characteristics mentioned above, we can establish the capability of nanoferrites for various catalytic applications, one being the synthesis of biodiesel through transesterification. Due to their magnetic behaviour, nanoferrites can easily be separated from the reaction mixture, and this property has motivated researchers to investigate heterogeneous catalysts for biodiesel production.

Biodiesel synthesis using heterogeneous nanoferrite catalysts

Nanoferrites have gained attention for heterogeneous catalysis applications in recent years. They exhibit the potential to lay the foundation of new technologies providing more efficient and greener catalysts for laboratory- and industrial-scale biodiesel synthesis. The following sections discuss the capability of various nanoferrites, their derivatives, and their composites for producing biodiesel through transesterification of soybean and canola oil.

Nanoferrites catalysts for transesterification of soybean oil

Soybean oil can be successfully converted into biodiesel through the transesterification process in the presence of methanol and $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoferrite catalyst. The $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles of crystallite size of ~17 nm can be synthesized using the combustion method. Around 92.1% of the biodiesel yield can be achieved using methanol to oil molar ratio of 9:1 and 2% of the catalyst loading by weight. At said catalyst loading, the transesterification reaction delivers optimum yield with 3 h of reaction time and the reaction temperature of 180 °C. The activation energy for the transesterification reaction, determined through the Arrhenius equation, comes around 67.4 kJ/mol. (Mapossa et al. 2020a). Other single-phase spinel structured nanoparticles, such as NiFe_2O_4 and $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$ can also be used as nanoferrite catalysts to produce biodiesel from soybean oil. The nanoparticles of NiFe_2O_4 and $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$, synthesized using the combustion method, can deliver a surface area value of 87.6 m²/g and 71.5 m²/g, and crystallite size of ~13 nm and ~20 nm, respectively. Due to comparatively higher saturation magnetization and higher acidity,

$\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$ provides a higher biodiesel yield of 94% compared to 49% by using NiFe_2O_4 . The $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$ nanoparticles exhibit an increase in magnetic property, acidity, and zeta potential due to present Zn^{2+} ions leading to a subsequent increase in biodiesel conversion with increasing Zn content (Mapossa et al. 2020b).

Nanoferrite particles of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ with crystallite size between 17 and 22 nm can be successfully used as heterogeneous catalysts and deliver soybean oil's conversion yield of up to $99.54 \pm 0.16\%$ through methyl esterification and up to $99.38 \pm 0.18\%$ through ethyl esterification. The catalyst can be magnetically extracted and reused for up to 3 cycles without exhibiting any substantial decrease in its catalytic activity. Optimum results can be obtained using 2% of the catalyst for carrying out esterification reaction at an alcohol/oil molar ratio of 12:1. The reaction gives a better yield when carried out for 1 h at 180 °C (Dantas et al. 2020). When the esterification of soybean oil is carried out for 1 h at the molar ratio of alcohol/oil as 15:1 and 160 °C, 3% of the $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoferrite catalyst of crystallite size of ~36 nm can deliver conversion yields of around 99.08% and 98.38% in methyl and ethyl routes, respectively. The catalyst for the same can be synthesized using the combustion reaction and exhibits a spinel structure with a surface area value of around 64.17 m²/g (Dantas et al. 2018). Cu^{2+} ions can be doped into $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoferrite catalysts for their application in methanol assisted transesterification process of soybean oil. A range of Cu doped $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoferrite catalysts with crystallite size ranging from 25 to 35 nm can be synthesized using a varying molar ratio of Cu^{2+} ions. The transesterification reaction can be carried for 1 h, at 180 °C with a methanol/oil molar ratio of 20:1 and 4% of catalyst dosage by weight. The catalyst's magnetic parameter with $\text{Cu}_x\text{Ni}_{0.5-x}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ composition (where x ranges from $0.0 \leq x \leq 0.4$ in steps of 0.1) decreases with increasing value of Cu^{2+} ions, and this can be attributed to the diamagnetic nature of copper. Figure 7 represents the effect of wt.% of copper in the nanoferrite catalyst composition on biodiesel yield (Dantas et al. 2017).

The transesterification and esterification reaction of soybean oil can be carried out using $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Ni}_{0.2}\text{Cu}_{0.3}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoferrite catalysts via both methyl and ethyl routes. The optimum results can be obtained when the reaction is carried out with an alcohol/oil molar ratio of 12:1, at 180 °C, and 1 h of reaction time. Both catalysts exhibit an inverse spinel-type phase. In the esterification process, using $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles, the biodiesel yield of 91.4% and 77.8% can be acquired through methyl and ethyl routes, respectively. The $\text{Ni}_{0.2}\text{Cu}_{0.3}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ catalyst can deliver a conversion yield of 75.1% through the methyl route and 65.1% through the ethyl route (Dantas et al. 2016). The inverse spinel-type phase of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoferrite catalyst with a crystallite size of 23 nm, surface area of 48.39

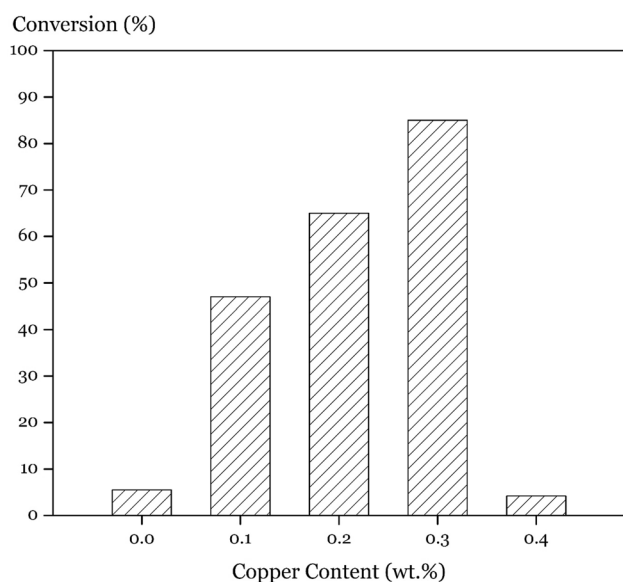


Fig. 7 Effect of the copper content in $\text{Cu}_x\text{Ni}_{0.5-x}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ composition on the biodiesel yield. The conversion yield tends to increase with increasing copper content till 0.3 wt.%. Increasing the copper content above 0.3% tends to decrease the conversion yield, suggesting that maximum conversion yield can be achieved using $\text{Cu}_{0.3}\text{Ni}_{0.2}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ composition as catalyst (Reproduced by permission from Ref. (Dantas et al. 2017), License Number 4923040589714, Copyright 2017, Elsevier)

m^2/g , and saturation magnetization value of 55 emu/g can be successfully used for the conversion of soybean oil. The optimum process parameters that deliver the best yield are the alcohol/oil molar ratio of 20:1, a catalyst loading of 4%, and when the reaction is carried out for 1 h at 160 °C (Dantas et al. 2015). Soybean oil can be esterified using methanol by using mixed nanoferrites catalysts of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, and $\text{Ni}_{0.2}\text{Cu}_{0.3}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ composition. The esterification reaction can be carried out for 1 h with a methanol/oil molar ratio ranging from 6:1 to 12:1 and catalyst loading of 2%. The reaction temperature delivering optimum result is 180 °C. As high as 92% of biodiesel yield can be obtained using $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles due to their higher catalytic activity (Silva et al. 2014).

When pure $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoferrites doped with 0.4 mol of Cu^{2+} ions are used for methyl transesterification of soybean oil, a conversion rate of around 13% and 50% can be obtained, respectively. The particle size of 23 nm and 62 nm for $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Cu}_{0.4}\text{Ni}_{0.1}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoferrite particles can deliver a surface area of 48.89 m^2/g and 18.06 m^2/g , respectively. The inclusion of Cu^{2+} ions in the composition increases biodiesel production by 26% due to its higher catalytic activity. The reaction duration also decreases, along with increased stability and combustion flame temperature because of Cu^{2+} ions in the catalyst composition (Dantas et al. 2014).

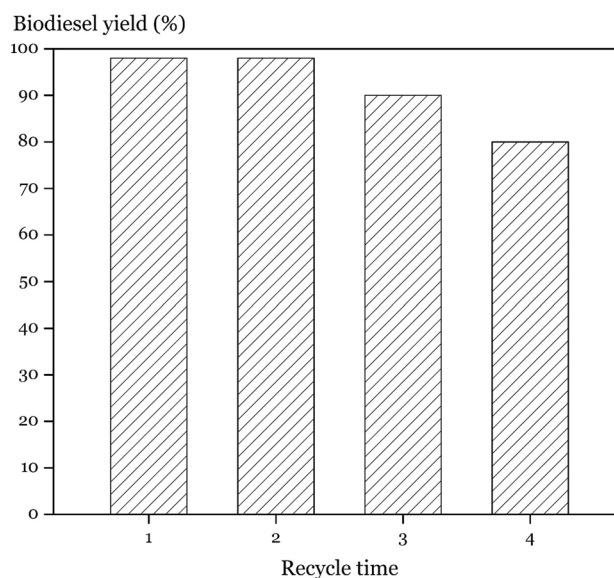


Fig. 8 Recycling capability of $\text{CaO}@ \gamma\text{-Fe}_2\text{O}_3$ nanocatalyst. The biodiesel yield tends to decrease as the catalyst is reused. This observed tendency suggests that the chemical activity and catalytic potential decreased with multiple reuses of the catalyst. (Reproduced by permission from Ref. (Shi et al. 2017), License Number 4923080238099, Copyright 2017, Elsevier)

The transesterification of soybean oil using methanol and $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoferrite catalysts doped with Cu^{2+} ions in the range of 0.1 and 0.4 mol. The reaction can be carried out with 4% catalyst loading by weight with an alcohol/oil molar ratio of 20:1, at 160 °C for 2 h. The addition of 0.4 mol of Cu^{2+} ions in the catalyst composition delivers a conversion rate of around 50.25%. This conversion rate can be credited to the higher surface area of 23.49 m^2/g and a particle size of 47.64 nm (Dantas et al. 2013).

Ferrite-based solid-base magnetic catalyst can be prepared with and without KNO_3 for the transesterification of soybean oil with methanol. The magnetic core supports CaO , and nanoparticles of $\text{CaO}@ \gamma\text{-Fe}_2\text{O}_3$ and $\text{CaO}@$ hematite Fe_2O_3 can be synthesized. The synthesized magnetic $\text{CaO}@ \gamma\text{-Fe}_2\text{O}_3$ catalyst delivers a high conversion yield of around 98.8%, owing to higher basicity than $\text{CaO}@$ hematite Fe_2O_3 . Such a higher yield can be obtained with an alcohol/oil molar ratio of 15:1, 2% of catalyst loading, 3 h or reaction time, and 70 °C temperature. The $\text{CaO}@ \gamma\text{-Fe}_2\text{O}_3$ magnetic nanocatalyst exhibits better catalytic performance for biodiesel production and can be reused up to 4 times without a substantial decrease in the conversion yield, as illustrated in Fig. 8 (Shi et al. 2017).

Soybean oil can be transesterified to produce biodiesel using a magnetic solid-base catalyst. i.e., $\text{K}/\text{ZrO}_2/\gamma\text{-Fe}_2\text{O}_3$ of particle size between 15 and 25 nm. 5 wt.% of catalyst amount along with methanol/oil molar ratio of 10:1. A biodiesel conversion yield of above 93% can be obtained

by carrying out a transesterification reaction for 3 h and at 65 °C. The synthesized nanocatalyst is ferromagnetic and retains its catalytic activity even after reusing 6 times. A significant decrease in biodiesel yield can be observed if the reaction temperature is decreased to 50 °C from 65 °C. If the methanol/oil molar ratio is reduced to 4:1, the biodiesel conversion yield drops to 48.5% (Liu et al. 2017). The CaO-coated magnetic nanoparticles, i.e., $\text{MgFe}_2\text{O}_4/\text{CaO}$, can successfully be used to produce soybean biodiesel through transesterification with high efficiency. The optimum reaction parameters for achieving around 98.3% of biodiesel conversion are 10 wt.% of catalyst loading, a methanol/oil molar ratio of 12:1, 5 h of reaction time, and at the reaction temperature of 70 °C. The catalyst shows better water and acid resistance and can be reused ~5 times without substantial reduction in the catalytic potential. Increasing the magnitude of reaction parameters tends to decrease the yield of the biodiesel conversion. A significant reduction in the biodiesel yield can be observed by increasing the catalytic loading from 1 to 3%, as shown in Fig. 9 (Liu et al. 2016). The CaO-doped CoFe_2O_4 magnetic solid-base nanocatalyst can be synthesized using the hydrothermal method for transesterification of soybean oil. The catalyst shows remarkable magnetic strength, excellent basicity, weaker hygroscopicity, and enhanced wettability compared to $\text{CaO}/\text{ZnFe}_2\text{O}_4$ and $\text{CaO}/\text{MnFe}_2\text{O}_4$, as represented in Fig. 10. A high yield of 87.4% can be achieved for a methanol/oil molar ratio of 15:1 and catalytic loading of 1%. The reaction is to be carried out

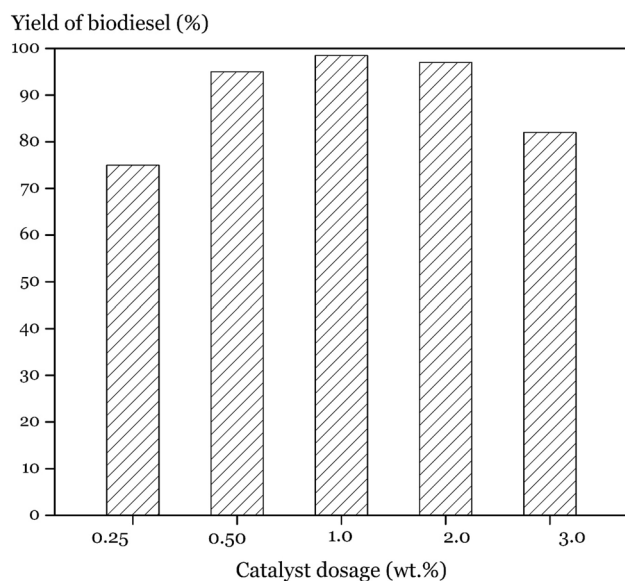


Fig. 9 Effect of catalyst loading on biodiesel yield. CaO-doped CoFe_2O_4 magnetic solid-base nanocatalyst delivers maximum conversion yields at a catalyst dosage of 1.0 wt.%. Catalyst loading less or more than 1.0% tend to decrease the biodiesel yield. (Reproduced by permission from Ref. (Liu et al. 2016), License Number 4923160723537, Copyright 2016, Elsevier)

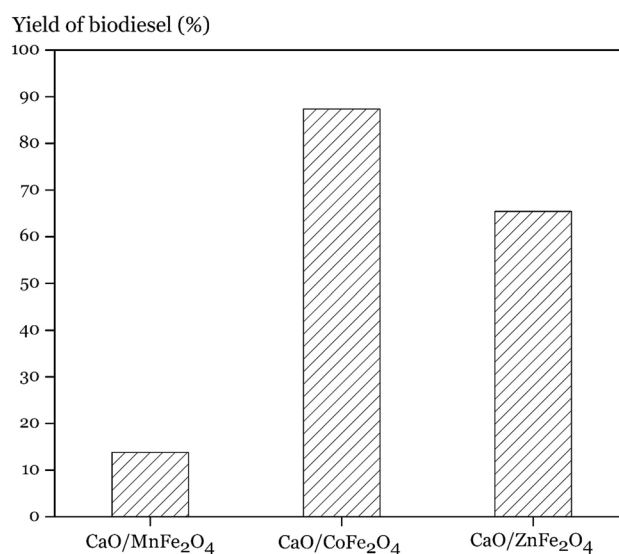


Fig. 10 Biodiesel yield using $\text{CaO}/\text{MnFe}_2\text{O}_4$, $\text{CaO}/\text{CoFe}_2\text{O}_4$, and $\text{CaO}/\text{ZnFe}_2\text{O}_4$ magnetic nanocatalyst at optimum reaction parameters. Maximum biodiesel yield can be achieved using $\text{CaO}/\text{CoFe}_2\text{O}_4$, whereas using $\text{CaO}/\text{MnFe}_2\text{O}_4$ delivers minimum conversion yield with a catalytic loading of 1.0 wt.% and 15:1 methanol/oil molar ratio. (Reproduced by permission from Ref (Zhang et al. 2014), License Number 4923171452271, Copyright 2014, Elsevier)

at 70 °C and for 5 h for maximum conversion. The synthesized $\text{CaO}/\text{CoFe}_2\text{O}_4$ catalyst shows reusability for up to 5 cycles of transesterification (Zhang et al. 2014).

We conclude that various nanoferrite compositions and their composites can be used as heterogeneous catalysts to achieve a more than 90% biodiesel conversion yield. The reviewed research suggests that most heterogeneous catalysts can be recovered from the reaction mixture without substantial loss in the catalyst mass. The heterogeneous catalysts can also be reused up to 4 times without observing any significant loss in their catalytic potential. Methanol performs better as alcohol for the synthesis process. However, using methanol as a reaction ingredient limits the maximum reaction temperature due to its low boiling point of ~65 °C. The use of excess alcohol favours the transesterification reaction, and therefore, the preferred alcohol/soybean oil molar ratio is between 12:1 and 16:1.

Nanoferrites catalysts for transesterification of canola oil

Magnetic Fe_3O_4 nanoparticles loaded with calcium aluminate can be synthesized to provide high catalytic activity and a biodiesel yield of around 99% from canola oil under standard conditions. These $\text{Ca}/\text{Al}/\text{Fe}_3\text{O}_4$ nanoparticles deliver the best performance at a Ca to Fe molar ratio of 5:1 with a calcination temperature of 600 °C and a calcination duration of 6 h. An increase in these reaction parameters tends

to reduce methyl esters yield significantly. The Ca/Al/Fe₃O₄ nanoparticles offer a high recovery rate through magnetic separation and retain their catalytic activity even after 5 cycles (Tang et al. 2012). The transesterification of canola oil can be achieved using KOH impregnated ZSM-5-Fe₃O₄ zeolite nanoscale magnetic catalyst. The biodiesel synthesis process can be optimized by carrying out the reaction with a methanol/oil molar ratio of around 12.3. The catalyst loading of about 9% can deliver a yield of approximately 94% after about 210 min of reaction time at 65 °C. The catalyst can be separated using an externally applied magnetic field, retain its catalytic potential, and be reused for up to five cycle processes. Figure 11 represents the biodiesel yield variations based on the wt.% of KOH loading on the ZSM-5-Fe₃O₄ zeolite nanoscale magnetic catalyst (Rezayan and Taghizadeh 2018).

A high transesterification yield, i.e., > 95% from canola oil to produce biodiesel, can be achieved using CaO/NaY-Fe₃O₄ magnetic nanocatalyst. The methyl esters of canola oil can be obtained within a reaction time of around 5 h via transesterification reaction, carried out at a temperature of 65 °C. The methanol to oil molar ratio can be ranged between 6 and 10, and catalyst loading can be varied between 4 and 5.5%. The biodiesel production yield of 85–95% can be obtained between these ranges using CaO/NaY-Fe₃O₄ magnetic nanocatalyst (Firouzjaee and Taghizadeh 2017). Transesterification of canola oil can be carried out using Li/Fe₃O₄

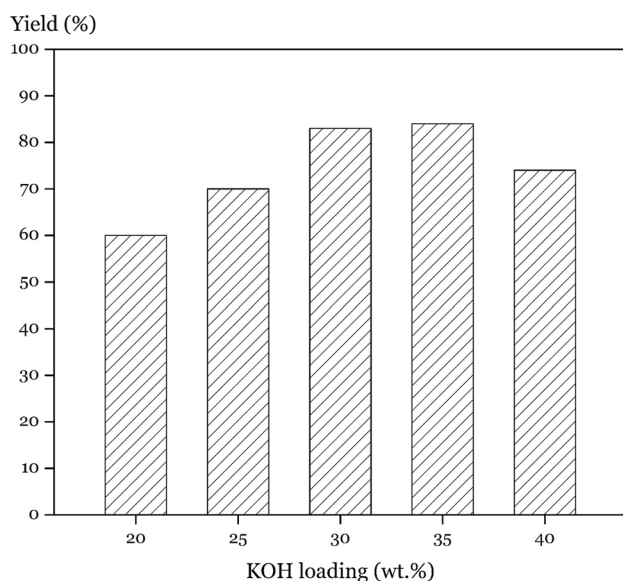


Fig. 11 Effect of KOH wt.% on biodiesel yield. The biodiesel yield increases with increasing KOH on the ZSM-5-Fe₃O₄ zeolite nanoscale magnetic catalyst up to 35 wt.% and decreases with further increase. Catalyst loading of 9% gives a biodiesel yield of ~94% after a reaction time of 210 min. (Reproduced by permission from Ref. (Rezayan and Taghizadeh 2018), License Number 4922620583355, Copyright 2018, Elsevier)

and Li/ZnO-Fe₃O₄ with a molar ratio of 3:1 and a small catalyst wt.% loading of 0.8. A high yield of 99.8 ± 0.2% can be obtained within a reaction time of 35 min and at a reaction temperature of 35 °C by using ultrasonic irradiation. The magnetization characteristics and catalytic potential of the catalyst remain significant even after multiple reaction cycles. The methanol/oil molar ratio for the reaction is 12:1 to achieve a conversion yield of above 99%. Keeping the reaction temperature limited to around 35 °C avoids the issue of saponification of the triglycerides. The reaction time and reaction temperature can be decreased using synthesized catalysts with ultrasonic waves at 37 kHz frequency (Fallah Kelarijani et al. 2020). Mesoporous core-shell structured KOH/Fe₃O₄@γ-Al₂O₃ magnetic nanocatalyst can be synthesized to obtain a maximum biodiesel yield from canola oil under optimum conditions. The magnetic nanocatalyst exhibits magnetic characteristics and porosity with an average pore diameter of around 11.9 nm. The presence of pores facilitates a higher number of active sites for catalysis. The optimum conditions to achieve a maximum yield of 97.4% include a methanol/oil molar ratio of 16:1 and a catalytic loading of around 6.45% by weight (Ghalandari et al. 2019).

A range of KOH/Fe₃O₄@Al₂O₃ magnetic core-shell structure catalysts can be utilized to synthesize biodiesel from canola oil when synthesized by the wetness impregnation method. The magnetic nanocatalyst with 25 wt.% loading of Fe₃O₄ exhibits a higher surface area than 15 wt.% loading, but showed higher catalytic activity. Around 98.8% of biodiesel conversion can be achieved when the reaction is carried out with a 12:1 methanol/oil molar ratio, 4% catalyst dosage, and a reaction time of 6 h. The catalyst can be extracted by applying an external magnetic field and reused several times for the catalysis process (Kazemifard et al. 2018). Potassium impregnated Fe₃O₄-CeO₂ magnetic nanocatalyst can be synthesized to achieve the conversion of canola oil into biodiesel. Among varying wt.% of the potassium impregnation, 25 wt.% exhibited the best catalytic potential, as shown in Fig. 12. A conversion yield of around 96.13% can be achieved using 4.5 wt.% of potassium impregnated Fe₃O₄-CeO₂ loading with a methanol/oil molar ratio of 7:1. The reaction is carried out at 65 °C and 2 h, and the synthesized nanocatalyst can be reused for up to 5 cycles of transesterification reaction (Ambat et al. 2019).

Future scope and outlook

Even though researchers have achieved substantial conversion yields, the application areas of nanoferrites for catalysis in biodiesel production are not much explored. A handful of nanoferrites have been tried and tested, and those chosen nanocatalysts have indeed performed well. We conclude from the present study that Ni-Zn nanoferrites and doped

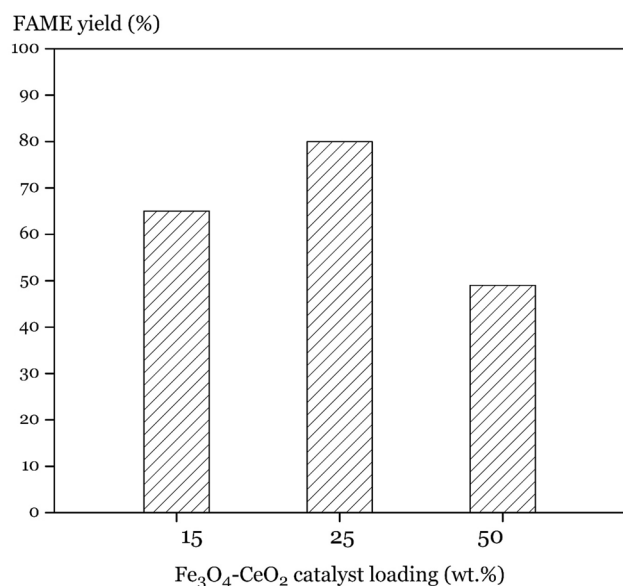


Fig. 12 Biodiesel conversion yield for different catalysts with varying potassium impregnation on $\text{Fe}_3\text{O}_4\text{-CeO}_2$ magnetic nanocatalyst. Catalyst loading of 4.5 wt.% of 25% potassium impregnated $\text{Fe}_3\text{O}_4\text{-CeO}_2$ magnetic nanocatalyst can achieve ~96% of conversion yield after the transesterification reaction is carried for 2 h at 65 °C. (Reproduced by permission from Ref. (Ambat et al. 2019), License Number 4923210053157, Copyright 2019, Elsevier). FAME: fatty acid methyl esters

Ni-Zn nanoferrites have been the preferred type of spinel nanoferrites for catalyst applications. Ions of various transition metal, poor metals, metalloids as well as alkali earth metals can be used as dopants to improve the performance of Ni-Zn nanoferrites. The nanoferrite catalysts of versatile compositions may exhibit specific and peculiar properties. For example, doping the base ferrite Fe_3O_4 with different transition metal ions, such as Cu^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , and Mn^{2+} , may alter the physical, chemical, structural, electrical, and magnetic properties of the doped nanoferrite. We endorse that a change in these properties affects the transesterification process's efficiency and, subsequently, the biodiesel quality and yield. The modified properties can be exploited in particular reactions to obtain higher yields in lesser times. The inclusion of dopants in the composition can also modify the available active sites, thereby changing the nanocatalysts' catalytic potential. The class of nanoferrites offers countless possibilities to design and synthesize specific nanoferrites with peculiar properties for biodiesel synthesis.

According to the authors, one area of future work is to load the conventional nanoferrites with dopants having specific magnetic properties. A diamagnetic dopant may provide a composite nanoferrite catalyst, which may have entirely different magnetic properties than a catalyst obtained by loading a paramagnetic dopant. This variation

in the catalyst's magnetic properties can be exploited to improve the biodiesel synthesis process's output. Further research is needed to formulate multifunctional magnetic nanocatalysts with a ferrite core and a base shell. Such nanocatalysts may offer the advantage of both magnetic catalyst and base catalyst, thereby delivering effective catalysis in addition to easier separation.

Another area that is less explored and demands much attention is applying ultrasonic or microwave irradiation during the transesterification process. Acoustic cavitation formation in the reactants upon applying the ultrasonic irradiation may increase the catalyst-reactant interaction, thereby increasing the catalytic potential of the magnetic nanocatalysts. The field of sonocatalysis must be explored to use nanoferrites catalysts as more dispersed particles in the reactants may significantly enhance the catalytic activity. Similarly, the rapid oscillation of molecules upon microwave irradiation may instigate catalyst interaction with the surrounding reactants as ferrites are known to absorb electromagnetic radiation such as microwaves. This enhanced contact may improve the efficiency of the nanoferrite catalysts along with thermal energy buildup in the solution due to molecular vibration.

We further advocate that many parameters and properties simultaneously influence and govern the yield of the ester conversion process for biodiesel production. Some of these parameters and properties have a strong direct or inverse relationship between their magnitude and biodiesel yield. However, the influence of some of these parameters can be negligible. Nonetheless, knowledge and understanding of the influence of these parameters and properties on the overall transesterification process' efficiency are indeed crucial to design an effective biodiesel production setup delivering maximized yields. Sections below present the authors' collective outlook on the influence of various parameters and properties on the overall biodiesel yield produced via the transesterification route.

Influence of reaction parameters on biodiesel yield

Researchers' investigations to produce biodiesel using nanoferrites as heterogeneous catalysts reveal significant dependencies of the reaction parameters on biodiesel yield. A few of these crucial parameters are catalyst loading, alcohol to oil molar ratio, reaction time, and reaction temperature. Each of these reaction parameters requires careful optimization to achieve maximum biodiesel conversion yield and quality. The catalyst present in the reaction offers active sites for the contact between the catalyst and the substrate leading to subsequent chemical reactivity. A higher catalyst loading offers more number of active sites available for catalysis. This phenomenon results in the enhanced catalytic activity, which further leads to increased biodiesel conversion yield

while the reaction time is significantly decreased. However, increasing the catalyst loading beyond a certain optimized amount leads to a subsequent increment in the alcohol-oil mixture's viscosity. Increment in the mixture's viscosity resists mixing and defers contact between the catalyst and the substrate, and demands additional catalyst separation energy. Results have concluded that the catalytic loading of 2–4% is optimal for appropriate biodiesel conversion.

We confirm that the alcohol to oil molar ratio in the mixture governs the rate of reaction kinetics. Higher alcohol to oil molar ratios compared to the stoichiometric ratio give better biodiesel yields. Lower ratios decrease the reaction kinetics rate and increase the reaction time. The stoichiometric alcohol to oil molar ratio is 3:1, but researchers have investigated the potential of molar ratios ranging from 6:1 to 20:1. Our observation state that at higher molar ratios than 20:1, it becomes exceedingly difficult to separate glycerol from the mixture, and thus, the biodiesel yield tends to decrease. The reaction temperature is a vital reaction parameter as it governs the biodiesel synthesis process's yield. The impact of the reaction temperature on the reaction output is twofold. Firstly, the increase in temperature increases the rate of reaction kinetic, thereby considerably speeding up the transesterification reaction and reducing the overall reaction time. The second critical effect of temperature is the decrease in the mixture's viscosity due to increased temperature. The decrease in viscosity increases the miscibility of liquid ingredients and allows for enhanced contact between the catalyst and the substrate. This phenomenon directly leads to reduced reaction times and better yields. However, the increment in the reaction temperature is limited by alcohols' low boiling temperature, especially methanol and ethanol. Reaction temperatures more than the boiling temperature lead to loss of alcohol in the mixture due to boil-off, subsequently increasing the synthesis process's cost. Similarly, the reaction time also affects the overall yield of the biodiesel synthesis. Since transesterification is a reversible process, higher reaction time than optimized for specific reaction parameters and nanoferrite catalyst tends to reverse the ester conversion reaction. This reversal of transesterification reaction eventually results in a decline in the overall biodiesel synthesis yield. Likewise, lesser reaction times than optimum fails to provide a sufficient period for the catalyst and the substrate to interact, thereby resulting in lesser overall biodiesel yield.

Influence of nanocatalysts' characteristics on biodiesel yield

Similar to the critical effect of various reaction parameters, various structural, morphological, chemical, and magnetic characteristics of the nanoferrite catalysts affect the overall efficiency of the biodiesel synthesis process in terms of

quality and yield. Nanoferrites are known to have at least one of their dimensions in nanoscale. This geometrical characteristic allows for the production of such heterogeneous catalysts that mimic the traits of homogeneous catalysts due to their nanoscale size. Such small crystallite size favours the high specific surface area, improving the dispersion and facilitating enhanced surface interactions between the catalyst and the mixture. Enhanced interactions subsequently lead to better yields. The nanoscale dimension of the ferrite catalysts leads to the availability of many active chemical sites, which supports the enhanced chemical activity of the nanoferrite catalysts. The characteristics mentioned above advocate that nanosized catalysts will facilitate better biodiesel yields than their microscale counterparts. The porosity of the catalyst is yet another factor that substantially affects the overall conversion yield. Porosity in the catalysts' structure leads to a significant increase in surface area available to form active sites, thereby favouring the catalytic performance. Enhanced porosity results in narrower interactions between the catalyst and the oil/alcohol mixture, and thus biodiesel yield increases. Another property that influences the catalysts' catalytic performance is the zeta potential, representing the largest number of +ve charges available on the solid surface. A higher number of +ve charges tends to attract a higher number of -ve charged -OH group counter ions, thereby increasing the catalytic activity on the surface. Any catalysts exhibiting a positive value of zeta potential would suggest the suitability of that catalyst for catalytic transesterification of the feedstock oil for biodiesel synthesis. A higher zeta potential value is also indicative of the stability of the nanoferrite catalysts, as the value of zeta potential represents the degree of electrostatic repulsion between similarly charged particles. A high degree of repulsion between particles corresponds to a low tendency of their agglomeration, conferring high chemical stability.

Similarly, the higher acidity of the catalysts results in better biodiesel yields. Higher Lewis or Brønsted acidity increases the catalyst's interaction capability, thereby favouring the nucleophilic attack on the carbonyl carbon and initiating the catalytic process. Another critical property that is equally influential and governs the overall efficiency of the transesterification is the magnetic characteristics of the nanoferrite catalysts. The higher saturation magnetization of nanoferrite catalysts can simply represent high recoverability of the catalyst from the mixture, minimizing catalysts' mass loss. High recoverability also supports the catalysts' reusability, making the whole biodiesel synthesis process through catalytic transesterification comparatively cost-effective. Nanoferrite catalysts with the high magnetic ability also exhibit higher activity due to enhanced attraction and strong ionic interactions among particles. These favourable characteristics also result in improved catalytic potential and stability of the nanoferrite catalysts for biodiesel production.

Conclusion

Since the first vehicle operated using biodiesel in 1938, continuous investigations are being conducted to obtain biodiesel's high-quality and high-quantity through the transesterification process. The exponential growth in the production and application of biodiesels has opened multiple opportunities to achieve sustainable energy generation. The transesterification process of biodiesel synthesis is favoured due to its simplicity and high conversion yields. The reaction is carried out in the presence of commonly available alcohol, i.e., methanol or ethanol, and does not require any sophisticated equipment or complex reaction conditions. The involvement of a catalyst decreases the reaction's activation energy and accelerates the process to deliver better biodiesel yields in lesser times. Depending on the type of catalyst, the reaction parameters and reaction output tend to differ substantially. Therefore, the selection of a suitable catalyst is a critical factor in biodiesel synthesis. Though homogeneous catalysts are proven to be more effective and deliver higher yields, heterogeneous catalysts offer the significant advantage of easier separation than homogeneous catalysts. The high catalytic activity of homogeneous catalysts can be attributed to being in a similar phase as the catalyst and the reactants interact at the molecular level. Heterogeneous catalysts lack this fundamental characteristic because of their defined and large particle size. The researchers address this notable limitation by exploring various types of nanoparticles to be used as catalysts to produce biodiesel.

The nanometer dimension of these particles allows for a higher surface area and availability of more active sites on the particle surface, facilitating enhanced interaction between catalyst particles and reactants. Furthermore, if these particles have ferrimagnetic properties, they facilitate easier separation from the reactants by only applying an external magnetic field. This tendency is a crucial advantage delivered by nanoferrite catalysts, as the nanoparticles can be recovered and reused multiple times, thereby enhancing the efficiency and cost-effectiveness of the synthesis process. The faster and effortless separation of the nanoferrite heterogeneous catalysts avoids the issue of emulsification and saponification along with reduced quantities of chemical wastewater produced post-reaction. All these advantages have attracted researchers' attention to use nanoferrite for catalysis in biodiesel production via the transesterification method.

In the present study, we report that nanoferrites extensively show the potential of being used as heterogeneous catalysts for the successful transesterification of soybean and canola oil. It is also apparent that in most cases, the

optimum methanol/oil molar ratio for the synthesis of biodiesel from soybean and canola oil ranges between 10:1 and 20:1. A molar ratio below and above this range tends to reduce the biodiesel production yield appreciably. The reaction temperature of 65 °C is best suited for the methanol assisted transesterification process since, above this temperature, the methanol in the reactant starts to evaporate. The optimum catalytic loading ranges between 2 and 4 wt.% of the oil, and below and above this range, the biodiesel yield tends to decrease. We also recognize that magnetic solid-base nanocatalyst offers better yields than magnetic solid-acid nanocatalysts.

The opportunities available in the domain of nanotechnology are limitless. We recommend that comprehensive research is needed to be carried out to investigate a variety of nanoferrite catalysts, their derivatives, and their composites for their application in the biodiesel synthesis processes. The production and use of large quantities of biodiesel for the energy generation and transportation sector's powerplants is the unavoidable need of the hour. The application of nanoferrites as heterogeneous catalysts is one of the keys that have the potential to open doors for rapid, cost-effective, and industrial-scale production of biodiesel to address the grave issues of depleting fossil-based fuel reserves and environmental pollution.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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