

Original Research

Catalytic Performance of CO:Ni Mixed Oxide Based Catalyst for Green Fuel Synthesis from Biomass Derived *Citrullus Colocynthis* Oil

Piyush Shrivastava [†], Jharna Gupta ^{*}, Rushil Bhatt [†], Aditi S. Vetal [†]

Department of Chemical Engineering, The Maharaja Sayajirao University of Baroda, Pratapgunj, Vadodara, Gujarat 390002, India; E-Mails: piyush.s-chemengg@msubaroda.ac.in; Jharnagupta-chemengg@msubaroda.ac.in; rushilbhattchemengg@msubaroda.ac.in; aditi.v-chemengg@msubaroda.ac.in

[†] These authors contributed equally to this work.

^{*} **Correspondence:** Jharna Gupta; E-Mail: Jharnagupta-chemengg@msubaroda.ac.in

Academic Editor: Lucília Graciosa de Sousa Ribeiro

Special Issue: [Advanced Catalysis for Green Fuel Production from Biomass and Wastes](#)

Catalysis Research

2025, volume 5, issue 1

doi:10.21926/cr.2501002

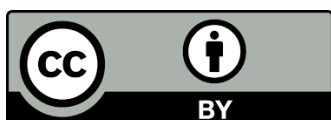
Received: September 18, 2024

Accepted: December 18, 2024

Published: January 08, 2025

Abstract

This study aimed to synthesize nickel oxide (NiO) and cobalt oxide (Co₃O₄) based catalysts for synthesizing biodiesel from *Citrullus colocynthis* oil. Cobalt-nickel mixed oxide catalysts made by co-precipitation technique with different Cobalt to Nickel ratios and named Co:Ni (50:50), Co:Ni (67:33), and Co:Ni (33:67). The Characterization of these synthesized catalysts was performed by XRD and SEM analysis. The transesterification process checked the catalytic activity of these catalysts, and it was found that Co:Ni (33:67) gave the maximum yield, i.e., 90%. The experimental conditions for the maximum yield of biodiesel were 65°C temperature, the Molar ratio of methanol to oil to be 9:1, the time required for reaction taken to be 2.5 h, and catalyst loading of 3.5 wt%. Co:Ni (33:67) exhibits strong catalytic activity and stability, making it a viable heterogeneous catalyst for biodiesel synthesis. Five recyclability studies were conducted in the present study. This research's novelty is synthesizing heterogeneous



© 2025 by the author. This is an open access article distributed under the conditions of the [Creative Commons by Attribution License](#), which permits unrestricted use, distribution, and reproduction in any medium or format, provided the original work is correctly cited.

catalysts with varying ratios of cobalt to nickel and comparing their catalytic performance in biodiesel production.

Keywords

Biodiesel; transesterification; heterogeneous catalyst; *Citrullus Colocynthis* oil

1. Introduction

As the demand for alternative fuels has increased in recent years, many researchers have attempted to find sustainable solutions, from commercial fuel to eco-friendly and renewable sources. A Better alternative to fossil fuels is biofuel, which can replace diesel with biodiesel as an eco-friendly fuel source [1]. Biodiesel has attracted significant attention owing to its significant advantages such as nontoxicity, high lubricity with renewable sources, sulphur-free nature, high flash point, oxygenated nature, and best biodegradable fuel alternative, which results in the reduction of greenhouse gases and demands finite petroleum resources [2, 3].

Both edible and non-edible seed oils have been identified as potential feedstock for biodiesel synthesis. While edible seed oils such as soybean, canola, palm, and sunflower are readily available, abundant, and contain high levels of oil [4, 5], their use as biodiesel feedstock raises concerns about food security and affordability. This is because diverting these oils from production can increase prices and limit supplies. Non-edible oils are increasingly being explored as alternative feedstocks for biodiesel production because they offer several advantages, including competition for food resources and speculative deployment of marginal lands [6]. Some non-edible oils commonly used for biodiesel include Thumba oil, Jatropha Oil, Tung Oil, Jojoba Oil, and Pongamia Oil. Recently, researchers have focused on increasing the efficiency and scalability of biodiesel synthesis from non-edible oil feedstocks as a renewable energy source [7, 8]. The utilization of non-edible oil in domestic use is nearly negligible because of its toxic components, which do not suit human health even when grown in forest regions and barren lands without much cultivation process, and is even its cost-effective than edible oil [9]. *Citrullus colocynthis* is increasingly being recognized for its potential as a biodiesel feedstock. Globally, *Citrullus colocynthis* oil production is relatively limited and often region-specific, with notable cultivation in countries such as India, parts of the Middle East, and North Africa. Its economic potential has gained attention for both industrial and pharmaceutical applications owing to the high quality of its fatty acids. *Citrullus colocynthis* plants are drought-resistant, with each fruit containing up to 1,000 seeds, making it an efficient source for oil extraction. *Citrullus colocynthis* seeds contain 22-53% oil, depending on the variety and growth conditions [10]. The oil yield per hectare can exceed 3,000 kg, making it comparable to or even higher than that of many traditional oilseed crops, such as soybean and rapeseed. The primary application of *Citrullus colocynthis* oil is biodiesel production. It is an eco-friendly alternative to fossil fuels, emitting fewer hydrocarbons and contributing to lower greenhouse gas emissions. This makes it an attractive option for sustainable energy initiatives [11, 12].

Homogeneous catalysts (NaOH, KOH, CH₃ONa, CH₃OK and H₂SO₄) are commonly used industrial catalysts because of their fast reaction rates under moderate conditions [13]. Homogeneous acidic or basic catalysts produce higher catalytic activity in biodiesel yield under mild operating conditions

[14]. However, some disadvantages, such as additional separation, purification steps, and soap formation in the reaction, require attention for synthesizing heterogeneous catalysts for biodiesel synthesis [15, 16]. Biodiesel production often uses heterogeneous catalysts. These solid catalysts offer two key advantages: effortless recovery from the reaction system and the ability to be reused multiple times. Researchers have explored a wide range of solid catalysts for this purpose, including metal oxides, combinations of different oxides, metal oxides treated with sulfates, carbon materials with sulfonic acid groups, ion exchange resins, heteropolyacids, and specific materials such as calcium oxide, nickel oxide, magnesium oxide, zeolites and biowaste catalysts (*Psidium guajava* L. leaves catalyst and *Parkia speciosa* catalyst) [17-21]. Heterogeneous catalysts offer several advantages in biodiesel production, including convenient separation from reaction components, reduced soap formation, and potential for catalyst recycling. However, homogeneous catalysts may require higher reaction temperatures and longer reaction times [22].

Transesterification was studied by most of the research as the best biodiesel production method, with glycerol as a secondary product from its feedstock [23]. Transesterification yields high-purity biodiesel with lower viscosity, making it more compatible with diesel engines than pyrolysis, microemulsion, or blending. It operates under milder conditions than pyrolysis, reducing energy costs and avoiding the stability issues observed in microemulsions. Unlike blending oils, which are chemically altered to produce biodiesel with consistent performance and lower emissions, Transesterification also produces glycerol as a helpful byproduct, which adds economic value [24]. This process involves the reaction of the oil with an alcohol in the presence of catalysts, which may be either homogeneous or heterogeneous.

A literature survey found that cobalt oxide has good basicity characteristics, high catalytic activity in the reaction mixture, and a surface area of $121.1 \text{ m}^2/\text{g}$. However, it is not widely used for biodiesel production through transesterification reactions [25]. Conversely, nickel oxide has gained significant interest because of its extensive surface area, cost-effectiveness, and potential porous structure [26]. Hence, mixed-metal cobalt and nickel oxide catalysts have emerged as effective heterogeneous catalysts for biodiesel production from *Citrullus colocynthis* oil. These catalysts offer enhanced alkalinity and specific surface area, increasing activity and stability during the transesterification reaction. Various mixed metal oxides, such as CaZnO , CaO-MgO , $\text{TiO}_2\text{-MgO}$, NaZrO_3 and CaMgO have been employed as catalysts in transesterification reactions [27-29]. However, no one has yet attempted to produce biodiesel using a catalyst based on varying Co and Ni ratios, specifically the Nickel cobaltite (NiCo_2O_4) catalyst. The advancement of heterogeneous catalysts based on cobalt and nickel shows promising results, as cobalt oxide demonstrates significant catalytic activity in the transesterification process and the potential for combined effects with nickel oxide to enhance durability and activity. The combination of nickel and cobalt within the spinel structure creates a synergistic effect, improving catalytic activity and stability. Nickel enhances hydrogenation activity, while cobalt contributes to oxidation-reduction properties, making the catalyst more effective for transesterification.

Therefore, this analytical research intends to synthesize the heterogeneous catalyst with different Co: Ni ratios and good catalytic activity for biodiesel synthesis from *Citrullus colocynthis* oil. The reaction parameters and reusability tests were also analyzed for biodiesel synthesis. Studies Fourier-Transform Infrared spectroscopy (FTIR) and gas chromatography (GC) were performed and interpreted to characterize the biodiesel. To characterize the biodiesel, studies using Fourier-Transform Infrared spectroscopy (FTIR) by FT-IR spectrometer (Perkin Elmer spectra two) in the

range of 400-4500 cm^{-1} and gas chromatography (GC) by gas chromatography (Model: Master GC Dani Instruments, Italy) with a capillary column of length 30 m, Inner diameter 0.32 mm and film thickness 0.25 μm were used for biodiesel analysis.

2. Materials and Methods

2.1 Materials and Chemicals

Citrullus colocynthis oil was purchased from a nearby market and research was performed using analytical-grade anhydrous methanol, cobalt oxide (Co_3O_4), and nickel oxide (NiO) from Merck Limited, Mumbai, India.

2.2 Characterization of Oil

Citrullus colocynthis oil was evaluated for quality parameters, as shown in Table 1, following the ASTM D6751 standard test method. These parameters included the density, acid value, saponification number, viscosity, and molecular weight. Kinematic Viscosity was measured using a Saybolt viscometer (temperatures range from 21°C to 99°C).

Table 1 Properties of *Citrullus colocynthis* oil used in the present study.

Properties of <i>Citrullus colocynthis</i> oil	Tested value	Standard values
Density (g/ml)	0.85	0.85-0.93
Acid value (mg of KOH/g of oil)	16.23	5-20
FFA (%)	9.115	1-10
Kinematic viscosity (Cst) at 40°C	33	30-45
Saponification value (milligram of KOH/g of oil)	176	Less than 210
Molecular weight (gram/mol)	870.0	860-890
Color	Light yellowish	Yellowish brown

2.3 Catalyst Synthesis

A co-precipitation method was employed to prepare the catalysts, as shown in Figure 1. The co-precipitation method prepared three different Co:Ni ratios and supported on zirconium dioxide (ZrO_2). The precipitate was aged at 60°C for 1 h. Subsequently, it was filtered using Whatman filter paper, rinsed with distilled water, and placed in a hot-air drying unit operating at 100°C. The dried material was calcined at 500°C for 3 h and placed in a desiccator for further study, as shown in Figure 1 [30]. Catalysts with various Co_3O_4 and NiO ratios were prepared and designated as the Co:Ni ratios as shown in Table 2.



Figure 1 (a) Catalyst Preparation (b) Catalyst Filtration (c) Prepared Catalyst.

Table 2 Synthesized catalyst composition with varying Co:Ni ratios.

Catalyst		Ratio
Co ₃ O ₄	NiO	Co:Ni
4.816 g	4.480 g	50:50
3.210 g	1.493 g	33:67
1.605 g	2.986 g	67:33

2.4 Characterisation of Catalyst

This investigation deployed various characterization techniques, including Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD), to gain insights into the catalysts' structure and behavior. Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) analysis were carried out using the FESEM FEI system (Nova Nano 450) and an X-Pert Pro powder analytical instrument, respectively.

2.5 Biodiesel Production by Transesterification Method

Using an H₂SO₄ acid catalyst, the esterification procedure was initially performed to lower the FFA content at 60-70°C. A two-necked flat-bottom flask with a magnetic stirrer, temperature sensors, and a reflux condenser was used in the experimental setup [31]. Before initiating the reaction, 100 milliliters of *Citrullus colocynthis* oil was heated to atmospheric pressure at 60°C. The methanol and oil reaction mixture was combined in a 6:1 molar ratio with a set amount (1 ml) of acid catalyst. A two-hour batch period was chosen to complete the esterification process. The esterification reaction mixture was moved to a colloquial step funnel for phase separation after the completion of the reaction. After phase separation, the upper phase containing the esterified ester was used for transesterification.

Finally, the transesterification reaction used different CO:Ni ratios as solid catalysts. The esterified oil mixture (100 ml) was first heated and poured into a similar flask that was already filled with a heterogeneous mixture of methanol to oil molar ratio (3:1-12:1) and catalyst (1.5-5.5 g) under vigorous stirring using a magnet bar. The transesterification reaction occurred between 0.5 and 3.5 hours, with a constant temperature of 65°C. Once the response was concluded, the product was transferred to a funnel to enable phase partitioning. The solid heterogeneous catalyst was then separated from the reaction mixture by applying centrifugal force for 20 minutes at 5,000 rpm. A colloquial step funnel was then used to separate the glycerol. FAME was then used for characterization. The experimental procedure is shown in Figure 2. Biodiesel yield was determined and calculated using Equation (1).

$$\text{Biodiesel Yield (\%)} = \frac{\text{Vol. of citrullus Biodiesel (ml)}}{\text{Vol. of citrullus coloynthis oil (ml)}} \quad (1)$$

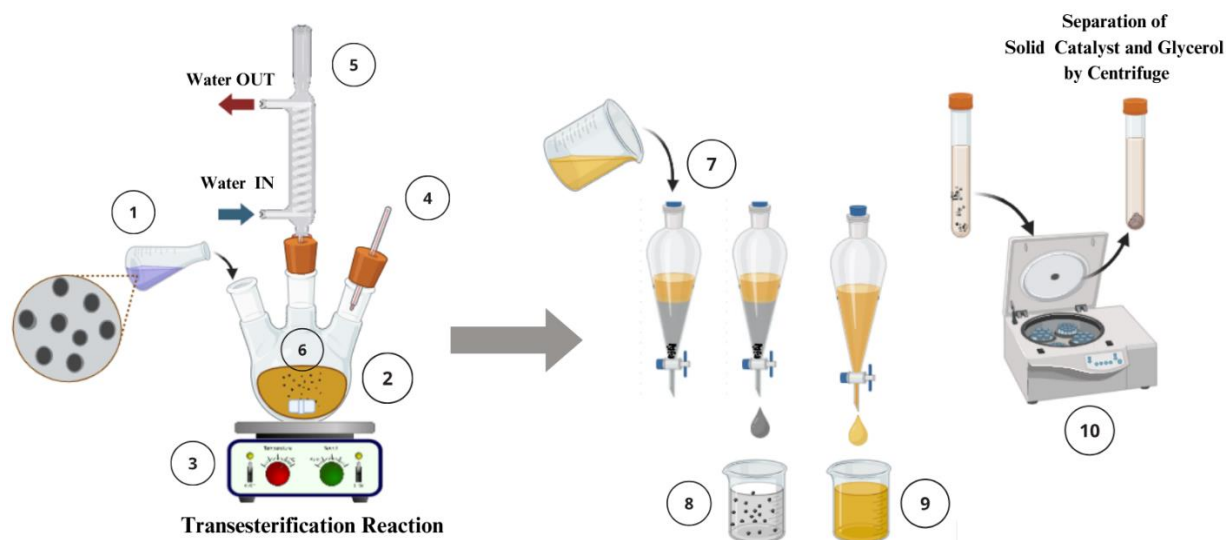


Figure 2 Biodiesel production employing the transesterification method. 1. Methanol and solid catalyst mixture. 2. Three-necked flask. 3. Magnetic stirrer with a hot plate. 4. Temperature-sensor. 5. Coil condenser. 6. Esterified *Citrullus colocynthis* oil. 7. Transfer the product mixture into a separating funnel. 8. Separation of glycerol with catalyst from biodiesel. 9. Collection of biodiesel. 10. Centrifuge process.

Repeated transesterification reactions evaluated the catalyst's recyclability. After each reaction, the solid catalyst was separated via centrifugation, dried, and calcined before reuse in the next cycle. The following optimized reaction conditions were maintained throughout: 3.5 wt% catalyst, 65°C reaction temperature, 2.5 h of time, and a 9:1 methanol-to-oil molar ratio.

2.6 Biodiesel Characterisation

Gas chromatography with a 30 m long and 0.25 mm thick capillary column was used to assess the purity of the biodiesel. Chromatographic variables were set as follows: detection: 280°C, injector: 240°C, column: 200°-232°C. First, two milliliters of hexane were used as the solvent to dissolve a 100 mg mixture of pure methyl esters (C8-C24). This solution was fed into the GC capillary column in 0.5-1 ml increments, and the elution times of each component were recorded.

3. Result and Discussion

3.1 Catalyst Characterisation

3.1.1 XRD Analysis

All XRD results show the presence of little traces of cobalt oxide (Co_3O_4) phase after the reaction of Co_3O_4 and NiO in different ratios and very low indication of Cobalt oxide phase left in the sample at $2\theta = 32.35^\circ, 36.69^\circ, 44.76^\circ, 50.1^\circ, 59.42^\circ$ and 67.55° as compared with the JCPDS card number 00-073-1701. A new phase of nickel cobaltite (NiCo_2O_4) was also found in comparison with JCPDS card number 47-1049. However, Co_3O_4 and NiCo_2O_4 phases have the same spinel structure but different lattice parameters (Co_3O_4 8.083 Å and NiCo_2O_4 8.111 Å) [31]. Therefore, it isn't easy to differentiate these two phases. Still, deep analysis of the lattice parameter confirms the presence

of NiCo_2O_4 phases in all the XRD graphs, mainly at $2\theta = 31.23$ and 38.30 as shown in Figure 3 [31]. Comparing all three graphs for different CO:Ni ratios, we found that the CO:Ni (33:67) ratio shows the major phase of NiCo_2O_4 , as shown in Figure 3(b). The other ratio i.e. CO:Ni (50:50) and CO:Ni (67:33) confirmed the presence of two phases i.e. NiCo_2O_4 and NiO as shown in Figure 3(a) and 3(c), respectively.

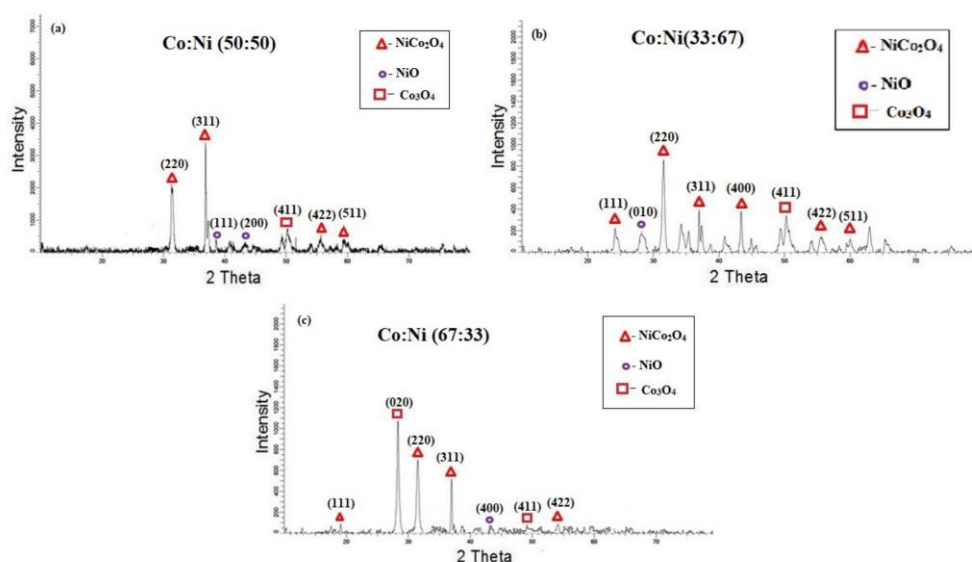


Figure 3 XRD analysis.

3.1.2 SEM Analysis

The surface topography of the sample with varying Co:Ni ratio are shown in Figure 4. The SEM images of all the prepared catalysts show irregular crystal structures with varied particle sizes. These different particle sizes are bound together by coalescence with different grain sizes and are distributed on the catalyst surface [31]. According to the literature, a smaller grain size of the catalyst results in a higher catalyst surface area. A higher surface area is responsible for catalytic activity. The observed surface morphology suggests a less porous structure because the porosity of the catalyst is directly influenced by its heat treatment. A smaller number of pores shows the higher treatment temperatures of the catalyst because the porous wall fractures at higher temperatures [32]. NiO peaks in each CO:Ni ratio catalyst occurred because of the thermal decomposition of NiCo_2O_4 during the calcination process above 400°C .

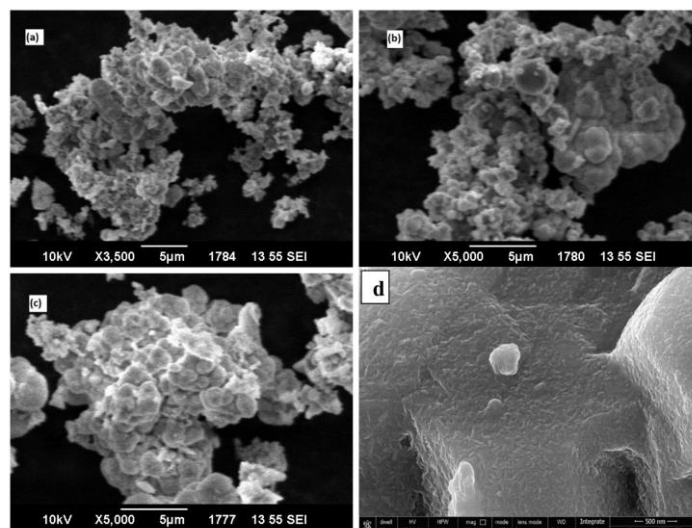


Figure 4 SEM image of three different catalyst based on variation of Co:Ni. (a) Co:Ni (50:50). (b) Co:Ni (67:33). (c) Co:Ni (33:67). (d) Reused catalyst after 5 runs.

3.2 Optimisation Study of Reaction Parameters

Figure 5(a) illustrates the effect of the methanol-to-oil molar ratio on biodiesel production. The biodiesel yield increased from 82% to 90%. It decreased from 90% to 85% when the methanol to oil ratio (mol/mol) was used from 6:1 to 12:1. The formation of a methoxy functional group on the catalyst surface steered the reaction towards the forward pathway. The biodiesel yield decreases when the methanol to oil ratio (mol/mol) increases to 12:1. Oil becomes more diluted owing to a higher amount of methanol, which results in a reversible reaction. Glycerol recovery becomes difficult and limits the biodiesel yield. Thus, the optimized value of methanol to oil ratio (mol/mol) was chosen to be 9:1 in this study [33].

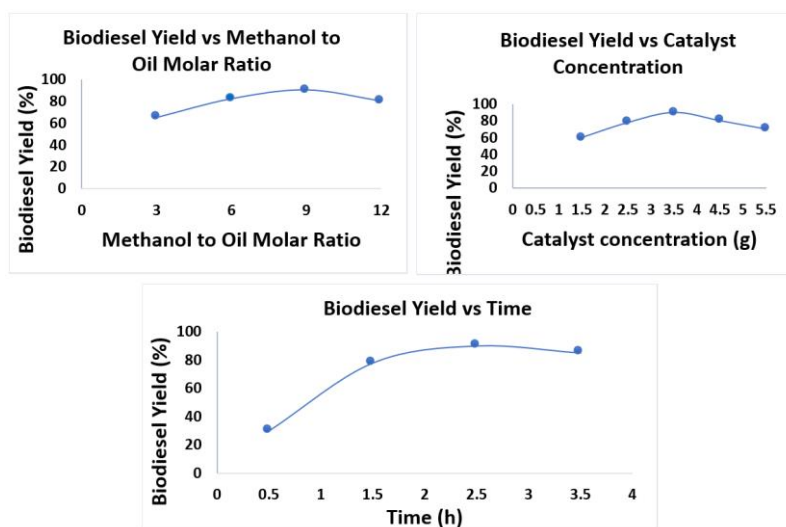


Figure 5 Optimization study of reaction parameters.

As seen in Figure 5(b), the transesterification processes were conducted using varying quantities of catalyst, ranging from 1.5 to 4.5 g. The graph shows that when the catalyst amount increases

from 1.5 to 4.5 g, biodiesel production also increases, and the biodiesel yield drops. Due to a high amount of catalyst, methanol and oil were not mixed properly, and separating the ester became difficult [34].

One of the most crucial elements in transesterification reaction is response time. Under ideal circumstances, the impact of the response time on biodiesel was investigated, as shown in Figure 5(c). The illustration shows that the biodiesel yield increased with increasing time and subsequently somewhat reduced after 2.5 h. This is because the saponification reaction reversibly produces soap, which hinders ester separation and lowers biodiesel production [35-38]. Thus, the ideal reaction time for the catalysts was 2.5 h. Several studies have documented biodiesel production using different heterogeneous catalysts, as outlined in Table 3. The reaction conditions obtained in this research were compared with similar research studies [39-48] from the literature (Table 3). Typically, the catalyst concentration is a little high for the transesterification reaction, possibly due to the neutralization of the acid used in the esterification step. Comparing biodiesel yield across different reaction conditions, it becomes evident that using a sufficient amount of catalyst (3.5 wt%) and methanol to oil molar ratio of 9:1 over 2.5 h resulted in the highest biodiesel yield and improved biodiesel properties.

Table 3 Investigation into the performance of other solid heterogeneous catalysts for biodiesel synthesis.

Heterogeneous catalyst	Oil	Temp (°C)	Alcohol to oil molar ratio	Time (h)	Catalyst conc. (wt %)	Yield (Y) Or Conversion (C) (%)	Reference
NiO	Jatropha oil	65	15:1	5	3	Y = 59.80	39
Ni doped ZnO	Palm oil	55	8:1	1	11	Y = 95.20	40
Ni-Ca HAP Solid acid catalyst	Waste frying oil	70	6.27:1	2	1.01	Y = 98.40	41
Anthill-eggshell Ni-Co mixed oxide	Waste frying oil	70	12:1	2	3	Y = 90.23	42
NiO	Acacia farnesiana seed oil	65	1:9	1	20 mg	Y = 96%	43
Ni/Fe Carbonate-fluorapatite	Waste cooking oil	70	8:1	2	10	Y = 97.5	44
CaO-Co	Microalgal	60	-	-	1.5	Y = 98%	45
Cobalt Oxide	<i>Chamaerops humilis</i> '	60	6:1	3	0.54	Y = 92%	46
MgO-CaO of Pharmaceutical Waste	'PISTACIA-TEREBINTHUS (PT) oil'	70	1:1.9 (vol:vol)	2	4.49	Y = 96%	47
MgO-CaO of Pharmaceutical Waste	Waste cooking oil	69.6	1:0.5 (vol:vol)	2	4.97	Y = 95.6%	48
CO-Ni mixed oxide	Citrullus cocynthis oil	65	9:1	2.5	3.5	Y = 90%	Present research work

3.3 Reuseability Study

In biodiesel industries, the reusability test of the catalyst plays a vital role from an economic perspective. As depicted in Figure 6, Several cycles of the transesterification process were used to examine the Co:Ni (33:67) catalyst's reusability. The transesterification reaction was repeated in the flask with the same volume of esterified oil and methanol added. As seen in Figure 6, the catalytic activity in terms of biodiesel yield decreases from 90% to 53%. No more studies were carried out as the tiny particles of the catalyst were broken up by vigorous stirring, and the little particles were released with the glycerol supernatant.

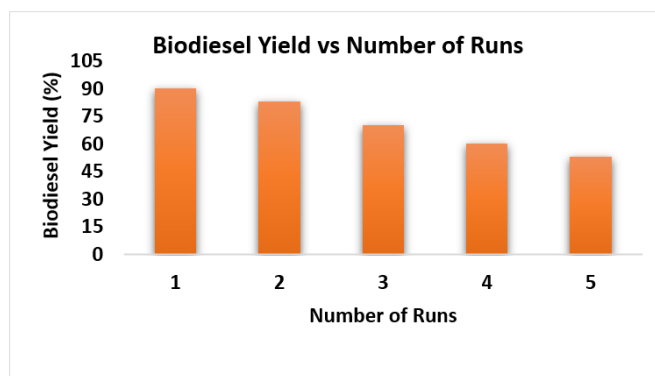


Figure 6 Reusability study.

The SEM image of the catalyst after being reused for 5 cycles, as shown in Figure 4(d), reveals the development of clusters and a rough and irregular surface, which reduces the catalyst activity.

3.4 Biodiesel Characterisation

The properties of *Citrullus colocynthis* oil biodiesel were analyzed and compared with the ASTM D6751 Standard test method, as illustrated in Table 4.

Table 4 Analyzed properties of *Citrullus colocynthis* oil biodiesel.

Properties	Unit	Biodiesel	ASTM std
Density	(g/ml)	0.85	0.860-0.900
Flash point	°C	153	130-170
Fire point	°C	181	140-215
Kinematic viscosity at 40°C	(Cst)	5.23	1.9-6.0
Cloud point	°C	9	-3 to 12
Pour point	°C	-3	-15 to 10

3.4.1 GC Characterisation

Gas chromatography analysis shows the fatty acid methyl ester (FAME) distribution in *Citrullus colocynthis* oil-based biodiesel. This analysis represents specific ester constituents, including oleic acid methyl ester, stearic acid methyl ester, palmitic acid methyl ester, and linoleic acid methyl ester. Gas chromatography (GC) was subsequently employed to authenticate the purity of the synthesized

biodiesel by its FAME profile with a standard reference [49]. Table 5 shows the different fatty acid compounds and their retention time in biodiesel products.

Table 5 Fatty acid compounds and their retention time in biodiesel product.

S. No.	Retention time (minute)	Compound name
1	8.053	Caprylic acid (C8:0)
2	10.087	Capric acid (C10:0)
3	11.993	Lauric acid (C12:0)
4	15.290	Myristic acid (C14:0)
5	19.760	Palmitic acid (C16:0)
6	24.553	Stearic acid (C18:0)
7	25.082	Oleic acid (C18:1)
8	26.347	Linoleic acid (C18:2)
9	30.223	Arachidic acid (C20:0)
10	35.127	Behenic acid (C22:0)

3.4.2 FTIR Analysis

The FTIR approach is advantageous over GC because it can evaluate entire samples, including the precipitated fraction, without additional processing. Figure 7 shows biodiesel's FTIR spectra obtained using Co:Ni (33:67) catalysts. According to published research, triglyceride and methyl ester have comparable chemical structures, which account for their similar spectra. The primary range in which the chemical structures of biodiesel and oil can differ is $1500\text{--}900\text{ cm}^{-1}$. The peak at 1436 cm^{-1} shows the presence of asymmetric stretching of -CH_3 in the biodiesel sample. Based on studies, the peaks in the $2800\text{--}3000\text{ cm}^{-1}$ regions and $1675\text{--}1725\text{ cm}^{-1}$, respectively, represent the stretching vibrations of $\text{CH}_3\text{(-CO-O-CH}_3\text{)}$ and the carbonyl group (-C=O). Additionally, the lack of a wide adsorption band in the $3300\text{--}2500\text{ cm}^{-1}$ range suggests that the biodiesel is dry, confirming the sample's dry phase (no moisture present) [49].

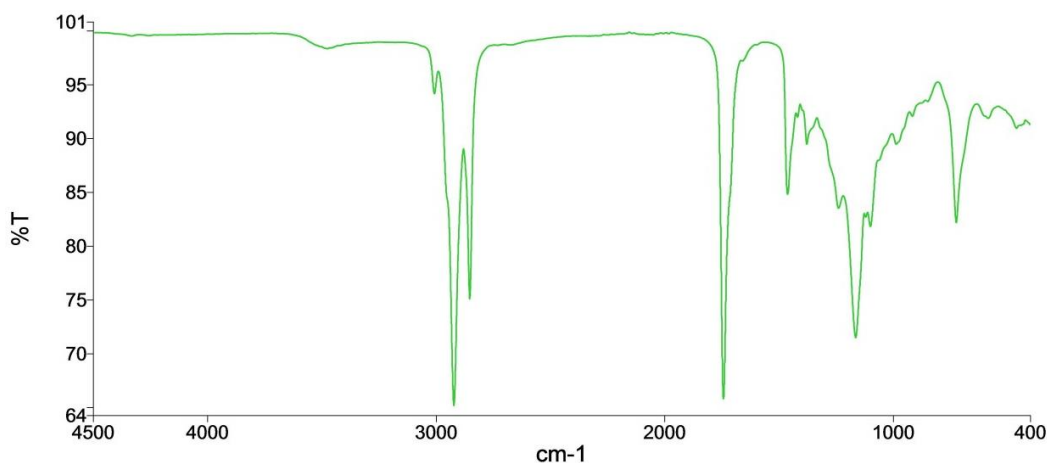


Figure 7 FTIR analysis of Biodiesel.

4. Conclusion

This study investigated the impact of varying Co: Ni ratios in nickel-based catalysts on biodiesel synthesis. Transesterification reaction tests and catalyst characterization techniques such as XRD and SEM were used to explain these effects. The transesterification reaction test indicates that the Co:Ni (33:67) catalyst exhibits the best catalytic activity for biodiesel synthesis among all the cobalt-nickel mixed oxide ratios. Compared to other catalysts primarily responsible for biodiesel synthesis and have proven to be excellent catalysts, the XRD results confirm that the NiO phase and NiCo₂O₄ spinel structure are significantly deformed. Nickel cobaltite (NiCo₂O₄) catalysts exhibit excellent properties for biodiesel production due to high surface area and porosity, synergistic Effect of Nickel and Cobalt, high thermal stability, enhanced electron transfer for faster and more efficient conversion of biodiesel, resistance to catalyst deactivation such as leaching and sintering. Characterized by an extensive surface area and superior catalytic behavior, the Co:Ni (33:67) spinel mixed metal oxide catalyst attained the maximum biodiesel yield (exceeding 90%) from non-food-grade *Citrullus colocynthis* oil, surpassing the performance of all other synthesized catalysts under specific reaction conditions, including a 2.5 h reaction time, a 9:1 methanol to oil molar ratio, a reaction temperature of 65°C, and a catalyst loading of 3.5% by weight. After five transesterification runs, the Co:Ni (33:67) catalyst's reusability test revealed that the biodiesel yields were higher than 50%.

Acknowledgments

The Maharaja Sayajirao University of Baroda, India provided support and funding for this work.

Author Contributions

Mr. Piyush Shrivastava, Mr. Rushil Bhatt and Miss Aditi S. Vetel have collected the data and written the manuscript. Dr. Jharna Gupta has given valuable suggestions for finalizing the manuscript.

Funding

The Maharaja Sayajirao University of Baroda, India provided support and funding for this work.

Competing Interests

The authors declare that they have no conflict of interest regarding this publication.

References

1. Eason G, Noble B, Sneddon IN. On certain integrals of Lipschitz-Hankel type involving products of Bessel functions. Philos Trans A Math Phys Eng Sci. 1955; 247: 529-551.
2. Rodionova MV, Poudyal RS, Tiwari I, Voloshin RA, Zharmukhamedov SK, Nam HG, et al. Biofuel production: Challenges and opportunities. Int J Hydrogen Energy. 2017; 42: 8450-8461.
3. Alalwan HA, Alminshid AH, Aljaafari HA. Promising evolution of biofuel generations. Subject review. Renew Energy Focus. 2019; 28: 127-139.

4. Ho DP, Ngo HH, Guo W. A mini review on renewable sources for biofuel. *Bioresour Technol.* 2014; 169: 742-749.
5. Sajjadi B, Raman AA, Arandiyan H. A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: Composition, specifications and prediction models. *Renew Sustain Energy Rev.* 2016; 63: 62-92.
6. Kumar A, Sharma S. Potential non-edible oil resources as biodiesel feedstock: An Indian perspective. *Renew Sustain Energy Rev.* 2011; 15: 1791-1800.
7. Patil PD, Deng S. Optimization of biodiesel production from edible and non-edible vegetable oils. *Fuel.* 2009; 88: 1302-1306.
8. Gui MM, Lee KT, Bhatia S. Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. *Energy.* 2008; 33: 1646-1653.
9. Banković-Ilić IB, Stamenković OS, Veljković VB. Biodiesel production from non-edible plant oils. *Renew Sustain Energy Rev.* 2012; 16: 3621-3647.
10. Pravin B, Tushar D, Vijay P, Kishanchand K. Review on *Citrullus colocynthis*. *Int J Res Pharm Chem.* 2013; 3: 46-53.
11. Nmila R, Gross R, Rchid H, Roye M, Manteghetti M, Petit P, et al. Insulinotropic effect of *Citrullus colocynthis* fruit extracts. *Planta Med.* 2000; 66: 418-423.
12. Hussain AI, Rathore HA, Sattar MZ, Chatha SA, Sarker SD, Gilani AH. *Citrullus colocynthis* (L.) Schrad (bitter apple fruit): A review of its phytochemistry, pharmacology, traditional uses and nutritional potential. *J Ethnopharmacol.* 2014; 155: 54-66.
13. Vicente G, Martinez M, Aracil J. Integrated biodiesel production: A comparison of different homogeneous catalysts systems. *Bioresour Technol.* 2004; 92: 297-305.
14. Atadashi IM, Aroua MK, Aziz AA, Sulaiman NM. The effects of catalysts in biodiesel production: A review. *J Ind Eng Chem.* 2013; 19: 14-26.
15. Tariq M, Ali S, Khalid N. Activity of homogeneous and heterogeneous catalysts, spectroscopic and chromatographic characterization of biodiesel: A review. *Renew Sustain Energy Rev.* 2012; 16: 6303-6316.
16. Semwal S, Arora AK, Badoni RP, Tuli DK. Biodiesel production using heterogeneous catalysts. *Bioresour Technol.* 2011; 102: 2151-2161.
17. Gupta J, Agarwal M, Dalai AK. An overview on the recent advancements of sustainable heterogeneous catalysts and prominent continuous reactor for biodiesel production. *J Ind Eng Chem.* 2020; 88: 58-77.
18. Di Serio M, Cozzolino M, Giordano M, Tesser R, Patrono P, Santacesaria E. From homogeneous to heterogeneous catalysts in biodiesel production. *Ind Eng Chem Res.* 2007; 46: 6379-6384.
19. Sarkar A, Nayak B, Joshi V, Paul B, Puzari A. An economic, and environmentally benign *Psidium guajava* L. leaves catalyst for biodiesel production at room temperature: Process optimization, and life cycle cost analysis. *Ind Crops Prod.* 2024; 222: 119609.
20. Anil N, Rao PK, Sarkar A, Kubavat J, Vadivel S, Manwar NR, et al. Advancements in sustainable biodiesel production: A comprehensive review of bio-waste derived catalysts. *Energy Convers Manage.* 2024; 318: 118884.
21. Sarkar A, Das P, Laskar IB, Vadivel S, Puzari A, Paul B. *Parkia speciosa*: A basic heterogeneous catalyst for production of soybean oil-based biodiesel. *Fuel.* 2023; 348: 128537.
22. Govindhan P, Prabhu NV, Edison Chandraseelan R, Dharmendira Kumar M. Technologies of biodiesel production: A state of the art review. *Pet Sci Technol.* 2024; 42: 339-356.

23. Saluja RK, Kumar V, Sham R. Stability of biodiesel-A review. *Renew Sustain Energy Rev.* 2016; 62: 866-881.
24. Otera J. Transesterification. *Chem Rev.* 1993; 93: 1449-1470.
25. Lim TH, Cho SJ, Yang HS, Engelhard MH, Kim DH. Effect of Co/Ni ratios in cobalt nickel mixed oxide catalysts on methane combustion. *Appl Catal A.* 2015; 505: 62-69.
26. Chen X, Yu S, Liu W, Zhang S, Liu S, Feng Y, et al. Recent advance on cobalt-based oxide catalyst for the catalytic removal of volatile organic compounds: A review. *Resour Chem Mater.* 2022; 1: 27-46.
27. Behnajady MA, Bimeghdar S. Synthesis of mesoporous NiO nanoparticles and their application in the adsorption of Cr (VI). *Chem Eng J.* 2014; 239: 105-113.
28. Taufiq-Yap YH, Lee HV, Yunus R, Juan JC. Transesterification of non-edible *Jatropha curcas* oil to biodiesel using binary Ca-Mg mixed oxide catalyst: Effect of stoichiometric composition. *Chem Eng J.* 2011; 178: 342-347.
29. Moura CV, Neres HL, Lima MG, Moura EM, Moita JM, Oliveira JE, et al. Cr/Al oxide as solid acid catalyst to afford Babassu biodiesel. *J Braz Chem Soc.* 2016; 27: 515-525.
30. Santiago-Torres N, Romero-Ibarra IC, Pfeiffer H. Sodium zirconate (Na_2ZrO_3) as a catalyst in a soybean oil transesterification reaction for biodiesel production. *Fuel Process Technol.* 2014; 120: 34-39.
31. Mahmood T, ul Haq S, Ahsan A, Syed WA. Using cobalt and nickel oxide nanoparticles for the conversion of solid kitchen waste into biofuel. *Curr Anal Energy Environ.* 2019; 1: 26-29.
32. Farokhi G, Saidi M. Catalytic activity of bimetallic spinel magnetic catalysts ($\text{NiZnFe}_2\text{O}_4$, $\text{CoZnFe}_2\text{O}_4$ and $\text{CuZnFe}_2\text{O}_4$) in biodiesel production process from neem oil: Process evaluation and optimization. *Chem Eng Process Process Intensif.* 2022; 181: 109170.
33. Ruhul AM, Kalam MA, Masjuki HH, Fattah IR, Reham SS, Rashed MM. State of the art of biodiesel production processes: A review of the heterogeneous catalyst. *RSC Adv.* 2015; 5: 101023-101044.
34. Islam A, Taufiq-Yap YH, Chu CM, Chan ES, Ravindra P. Studies on design of heterogeneous catalysts for biodiesel production. *Process Saf Environ Prot.* 2013; 91: 131-144.
35. Kawashima A, Matsubara K, Honda K. Development of heterogeneous base catalysts for biodiesel production. *Bioresour Technol.* 2008; 99: 3439-3443.
36. Gupta J, Agarwal M, Dalai AK. Experimental evaluation of the catalytic efficiency of calcium based natural and modified catalyst for biodiesel synthesis. *Int J Green Energy.* 2017; 14: 878-888.
37. Srivastava N, Kumar D, Rathour R, Srivastava M, Shrivastav AK, Mishra M, et al. Microbial synthesis of nickel-cobaltite nanoparticle for biofuel applications. In: *Recent developments in bioenergy research.* Amsterdam, Netherlands: Elsevier; 2020. pp. 349-362.
38. Gupta J, Agarwal M. Cost-effective biodiesel synthesis from waste marble powder as a green heterogeneous catalyst using *Pongamia pinnata* oil. *Catal Res.* 2023; 3: 013.
39. Mirzayanti YW, Asri NP, Marlinda L, I Muttaqii MA. Transesterification of *jatropha curcas* oil for biodiesel production over NiO catalyst. *J Phys Conf Ser.* 2021; 1833: 012041.
40. Baskar G, Selvakumari IA, Aiswarya RJ. Biodiesel production from castor oil using heterogeneous Ni doped ZnO nanocatalyst. *Bioresour Technol.* 2018; 250: 793-798.
41. Chakraborty R, Das SK. Optimization of biodiesel synthesis from waste frying soybean oil using fish scale-supported Ni catalyst. *Ind Eng Chem Res.* 2012; 51: 8404-8414.

42. Yusuff AS, Adeniyi OD, Azeez SO, Olutoye MA, Akpan UG. Synthesis and characterization of anthill-eggshell-Ni-Co mixed oxides composite catalyst for biodiesel production from waste frying oil. *Biofuel Bioprod Biorefin.* 2019; 13: 37-47.
43. Jan HA, Surina I, Saqib NU, Al-Sharif MS, Ali E, Wali S, et al. Application of recycled nickel-oxide nanoparticles for biodiesel synthesis from the non-edible seed oil of *Acacia farnesiana*. *Biofuels.* 2024; 15: 711-721.
44. Abukhadra MR, Dardir FM, Shaban M, Ahmed EA, Soliman MF. Spongy Ni/Fe carbonate-fluorapatite catalyst for efficient conversion of cooking oil waste into biodiesel. *Environ Chem Lett.* 2018; 16: 665-670.
45. Das V, Tripathi AM, Borah MJ, Dunford NT, Deka D. Cobalt-doped CaO catalyst synthesized and applied for algal biodiesel production. *Renew Energy.* 2020; 161: 1110-1119.
46. Rashidi S, Tahmasebi-Boldaji R, Baghbadarani AA, Baghdadi M, Tavakoli O, Karbassi A, et al. Biodiesel production through transesterification of waste *Pistacia-terebinthus* oil by pharmaceutical waste as a heterogeneous catalyst: A sustainable solution for reducing external costs. *Heliyon.* 2024; 10: e34404.
47. Ahmad M, Alruqi M, Zafar M. Cleaner production of biodiesel from novel and non-edible seed oil of *Chamaerops humilis* using recyclable cobalt oxide nanoparticles: A contribution to resilient and sustainable world. *J Clean Prod.* 2022; 369: 133378.
48. Tahmasebi-Boldaji R, Rashidi S, Rajabi-Kuyakhi H, Tahmasebi-Boldaji N, Baghdadi M, Karbassi A. Application of pharmaceutical waste as a heterogeneous catalyst for transesterification of waste cooking oil: Biofuel production and its modeling using predictive tools. *Biofuels.* 2024; 15: 415-431.
49. Siatis NG, Kimbaris AC, Pappas CS, Tarantilis PA, Polissiou MG. Improvement of biodiesel production based on the application of ultrasound: Monitoring of the procedure by FTIR spectroscopy. *J Am Oil Chem Soc.* 2006; 83: 53-57.