Novel Transition Metal Loaded Catalyst from Waste Biomass for Optimized Biodiesel Production

By

Laraib Aamir Khan

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Session 2020-2022

Supervised By

Dr. Rabia Liaquat

A Thesis Submitted to the U.S. – Pakistan Center for Advanced Studies in Energy in partial fulfillment of the requirements for the degree of

MASTERS of SCIENCE

in

ENERGY SYSTEMS ENGINEERING

U.S. –Pakistan Center for Advanced Studies in Energy (USPCAS-E)

National University of Sciences and Technology (NUST)

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THESIS ACCEPTANCE CERTIFICATE

Certified that the final copy of MS/MPhil thesis written by Ms. Laraib Aamir Khan, (Registration No. 00000359449), of U.S.-Pakistan Center for Advanced Studies in Energy (USPCAS-E), NUST has been vetted by the undersigned, found complete in all respects as per NUST Statues/Regulations, is in the allowable limits of plagiarism, errors, and mistakes and is accepted as partial fulfillment for the award of MS/MPhil degree. It is further certified that necessary amendments as pointed out by GEC members of the scholar have also been incorporated in the said thesis.

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Abstract

The decarbonization of transportation plays a crucial role in mitigating climate change, and biodiesel has emerged as a promising solution due to its renewable and eco-friendly nature. However, to maintain the momentum of the "green trend" and ensure energy security an ecologically friendly pathway is important to produce efficient biodiesel. In this work, activated carbon (AC) obtained from rice husk (RH) is hydrothermally prepared and modified through cobalt transition metal for catalyst support for the transesterification process. Various characterization techniques like Brunauer-Emmett-Teller (BET), Thermo-gravimetric analysis (TGA), Energy Dispersive Spectroscopy (EDS), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD) were utilized to analyze the created samples, and Gas Chromatography and Mass Spectroscopy (GC-MS) was utilized for analysis synthesized biodiesel. To optimize the transesterification process, Fatty Acid Methyl Esters (FAME) is produced by the conversion of waste cooking oil. Response Surface Methodology (RSM) is used to validate temperature (75 °C), the methanol-to-oil molar ratio (1:9), catalyst weight percentage (2 wt.%), and retention time (52.3 min). The highest conversion rate of waste cooking oil (WCO) to biodiesel was recorded at 96.3% and tested as per American Society for Testing and Materials (ASTM) standards. Based on the results, it was clear that cobalt-loaded Rice husk-based green catalyst enhanced catalytic activity and yield for biodiesel production at the industrial scale.

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Keywords: *Activated carbon, Heterogeneous catalyst, hydrothermal carbonization, transesterification, biodiesel, response surface methodology (RSM)***)***

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"Novel Transition Metal Loaded Catalyst from Waste Biomass for Optimized Biodiesel Production." ***Laraib Aamir Khan[1], Rabia Liaquat[1,*], Muhammad Usman Khan[1], Abdul Basit[1]***

Brazilian Journal of Chemical Engineering (Under Review) (IF = 1.772)

List of Abbreviations

Abbreviation:	**Description:**
AC	Activated Carbon
AC-Co	Cobalt-loaded Activated Carbon
ASTM	American Society for Testing and Materials
BD	Biodiesel
BBD	Box Behnken Design
BET	Brunauer Emmett Teller
C_0	Central Points
CCD	Central Composite Design
CN	Cetane Number
FFA	Free Fatty Acid
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography-Mass Spectrometry
GCV	Gross Calorific Value
GHG	Greenhouse Gases
HHV	Higher Heating Value
HTC	Hydrothermal Carbonization
HCL	Hydrochloric Acid
RH	Rice husk
RHAC	Rice husk Activated Carbon
RHAC-Co	Cobalt-loaded Rice husk Activated Carbon
RSM	Response Surface Methodology
SEM-EDS	Scanning Electron Microscope and Energy Dispersive Spectroscopy
WCO	Waste Cooking Oil

XRD	X-Ray Diffraction
TGA	Thermo-gravimetric Analysis
wt. %	Weight percent %

Chapter 1 Introduction

1.1 Background

Global transportation emissions have risen at an alarming rate in recent years, with an annual increase of 1.6% [1]. To meet the goals set by the Paris Agreement, which aims to keep global temperatures at a 2 °C increase, drastic measures must be taken to reduce overall transportation demand and decarbonize the remaining demand. While progress in this area has lagged behind other sectors [2], however, advancements in fuels and automotive engineering, as well as pressure to combat climate change, suggest a brighter future. One way to achieve deep emission reductions is through a combination of decarbonizing fuels and vehicle technologies. Some options for reducing emissions include switching to electric or hybrid vehicles, using biofuels instead of fossil fuels, and creating "electro-fuels" or carbon capture and utilization (CCU) fuels [3].

Currently, liquid biofuels are a practical solution for the decarbonization of transport as they can be incorporated into existing infrastructure and technologies that offer a way to gradually lower emissions for the current vehicle fleet and sectors where there are no viable alternatives to liquid fuels such as freight [4], maritime, and air transportation [5]. By switching to renewable biomass resources instead of petroleum, we can take a step towards sustainable development and better management of greenhouse gases. The implementation of biofuels that are derived through non-eatable lignocellulosic materials and waste are 2nd generation of fuels and has huge potential as they can offer massive volumes of low-GHG hydrocarbon fuels, whilst also avoiding the problems that plagued first-generation biofuels [3, 6]. Decarbonization of transportation is a vital step in addressing climate change, and one promising solution is the use of biodiesel [7].

Various plant-based sources like waste cooking and vegetable oil along with fats from animals give rise to the production of a sustainable and renewable fuel named biodiesel. Unlike traditional fossil fuels, biodiesel has a lower carbon footprint and can help reduce emissions from transportation. Additionally, currently used diesel can be replaced by biodiesel without requiring any adjustments [8-10], making it an economical and easily implementable resolution for decarbonizing transportation. A wide variety of vegetable oils like sunflower, rapeseed, palm, soybean, and castor oils, can all be utilized as feedstocks in the manufacturing process. The efficiency and effectiveness of the conversion process can be influenced by the choice of catalyst used [11-15].

Edible oil that has been utilized for cooking purposes in restaurants and hotels but is now obsolete is defined as waste cooking oil (WCO) in the current investigation. Furthermore, utilizing WCO as a substrate in the process of producing biodiesel not only encourages environmental conservation by minimizing waste but also has the possibility of decreasing expenses associated with waste management. There are three primary advantages to producing biodiesel from excess cooking oil, namely financial benefits, ecological benefits, and waste management benefits [16-18]. Improper disposal of WCO can negatively impact water quality and harm fish populations, other aquatic life, and local communities [19]. Heterogeneous catalysts have gained attention increasingly as a substitute method for manufacturing biodiesel. [20]. This is because homogeneous catalysts have limitations, elevating the significance of research into heterogeneous catalysts for biodiesel [21]. Several benefits can be gained by employing heterogeneous catalysts such as easy product separation, reusability, and minimal environmental impact during production. In recent years, there has been a growing fascination with utilizing waste materials as catalysts. Waste biomass obtained from various industries such as farming, sewage, mining, and metal fabrication are among the most readily available sources for this purpose. Using agricultural waste for catalytic production can reduce or eliminate the financial and environmental costs associated with disposal, making it a practice with many potential applications. In compared to conventional catalysts, rice husk (RH), a commonly accessible and underutilised unwanted products of rice milling, can minimise the cost of biodiesel synthesis and ease environmental problems that relate to waste disposal [11].

Several important factors, aside from the catalyst, are integral in enhancing and maximizing the yield of biodiesel production. Numerous optimization techniques are at our disposal, including factorial design, one-by-one testing, the Plackett-Burman design, genetic algorithms, artificial neural networks, and response surface methodology (RSM). Several research studies have shown that using a response surface approach can significantly improve the production of biofuels. This approach involves analyzing the interactions between different process parameters and identifying the optimal combination for maximum yield. By studying the relationship between the inputs and outputs, RSM can help identify the ideal process conditions and make the production process more efficient. As a result, this approach can lead to higher production yields and improve the economic viability of biofuel production [10, 22, 23].

1.2 Problem Statement

The importance of creating biodiesel has been heightened due to the growing demand for sustainable energy sources that can be renewed. Despite the viability and eco-friendliness of traditional biodiesel production techniques as a substitute for diesel, they face obstacles in the form of expensive catalysts and the limited availability of oil raw materials. The growing fascination with biodiesel underlines its promise as an environmentally-friendly alternative fuel source. This investigation aims to address the environmental issues related to waste management by utilizing rice husk and waste cooking oil as input materials and catalysts respectively to produce a greener and more effective fuel.

1.3 Research hypothesis

The production of biodiesel can be considerably improved with the use of structured materials that have higher catalytic activity. Structured materials like heterogeneous loaded catalysts provide a larger surface area which leads to faster reactions and a higher percentage yield. Additionally, the heterogeneity of these materials helps to mitigate several problems that may occur during the production of biodiesel, such as saponification, degradation of the catalyst, and issues with separating the biodiesel from the sample [24].

1.4 Objectives of study

The focus of this study is on finding a new way to convert used cooking oil into biodiesel by developing a novel Rice husk-derived heterogeneous catalyst (RHAC-Co). The catalyst that was created is analyzed using Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM). The synthesized biodiesel underwent additional characterization and was compared to ASTM criteria. Through the use of RSM, the transesterification process was fine-tuned to achieve a higher biodiesel yield. The parameters, including temperature (T), percentage of catalyst (%), the methanol/oil molar ratio (M:O), and duration, were all optimized. Finally, the optimal parameter settings and the dynamic relationship between process factors that affect product yield are provided. The primary goals of this research will be

- To synthesize a rice husk based heterogeneous solid catalyst (RHAC-Co) incorporating cobalt metal modification.

- To study how effectively the created catalyst can catalyze the transesterification process of WCO.

- To achieve a high conversion efficiency of WCO (96.3%) and analyze the independent variables (Temp, M:O ratio, catalyst conc. %, and reaction time) using RSM.

1.5 Scope of Study

The exploration of renewable energy sources has assumed substantial significance in contemporary times, given apprehensions about the decline in conventional fossil fuels, escalating petroleum expenses, and ecological predicaments. The utilization of biodiesel as a renewable energy source is a highly promising pursuit given its analogous qualities to conventional diesel, relating to viscosity, flash point, and cetane number. The utilization of WCO in the process of biodiesel production using transesterification is deemed highly advantageous on account of its wide availability, leading to the curtailment of feedstock, and the abatement of environmental apprehensions attributable to WCO disposal. Rice husk (RH), a plentiful and neglected by-product of rice milling, can be employed as a catalyst to substantially reduce the cost of biodiesel production when compared to conventional catalysts. Furthermore, this utilization of rice husk as a catalyst effectively addresses the environmental concerns associated with the disposal of waste products. Significance of using the RSM approach more frequently in the optimization of transesterification reactions to achieve more accurate outcomes. Fig. 1.1 shows the scope of this study in schematic form.

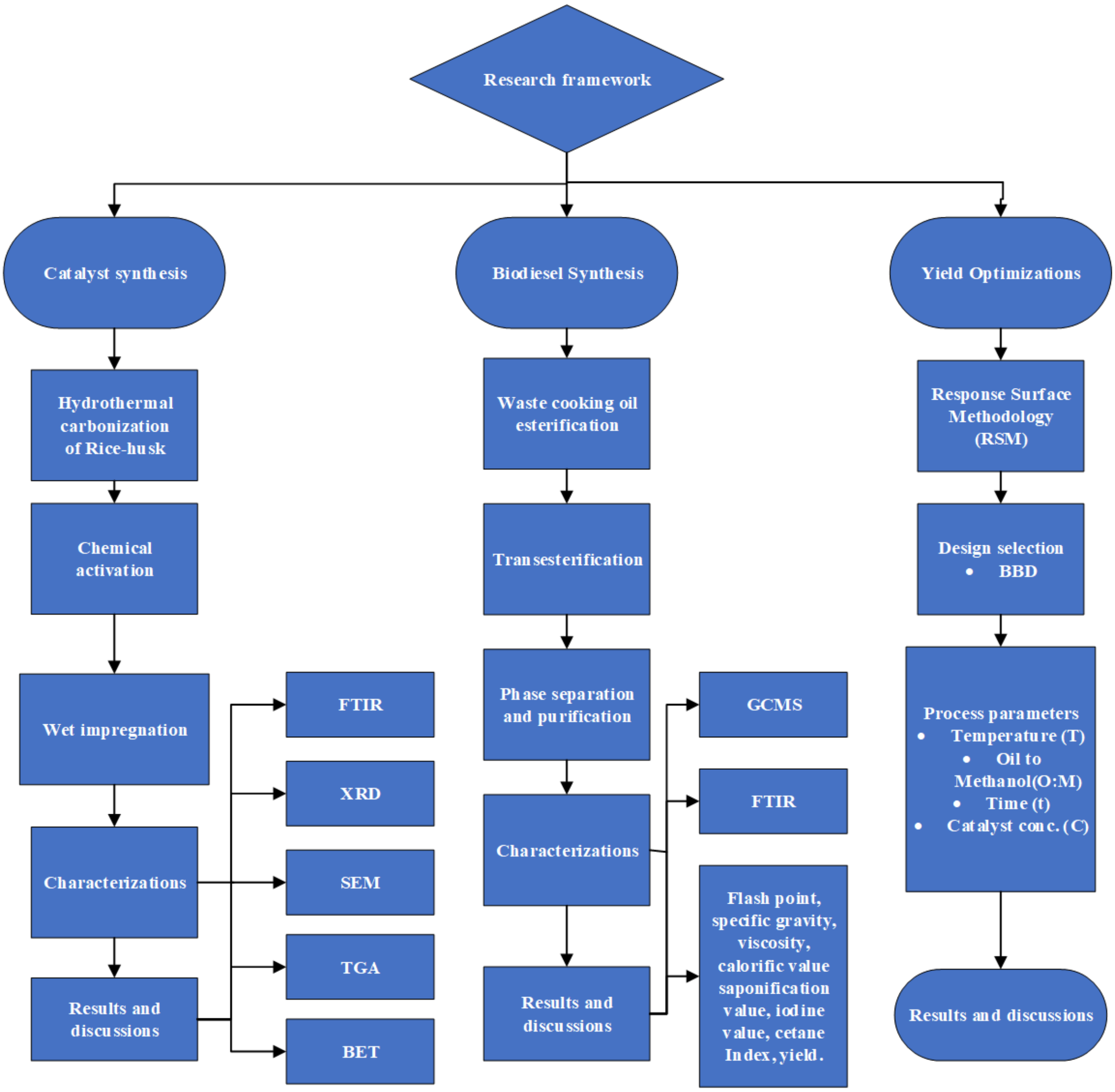

Fig. 1.1 Scope of the Research

1.6 Flow Chart of Thesis

The flow chart of the thesis is shown in Fig. 1.2. The study's goal was to evaluate how rice husk and waste cooking oil may be used more economically and sustainably rather than being thrown away in landfills or polluting the environment. For this goal, a literature review was conducted on existing feedstock data and utilization. A heterogeneous catalyst, derived from rice husk, was developed and subjected to comprehensive characterization via a range of analytical techniques, including SEM, BET, TGA, FTIR, and XRD. The RSM approach was also utilized to achieve more accurate outcomes of biodiesel yield. The catalytic prowess exhibited by the catalyst that was synthesized was also subjected to investigation. The data from the results were thoroughly reviewed in the results and discussion section.

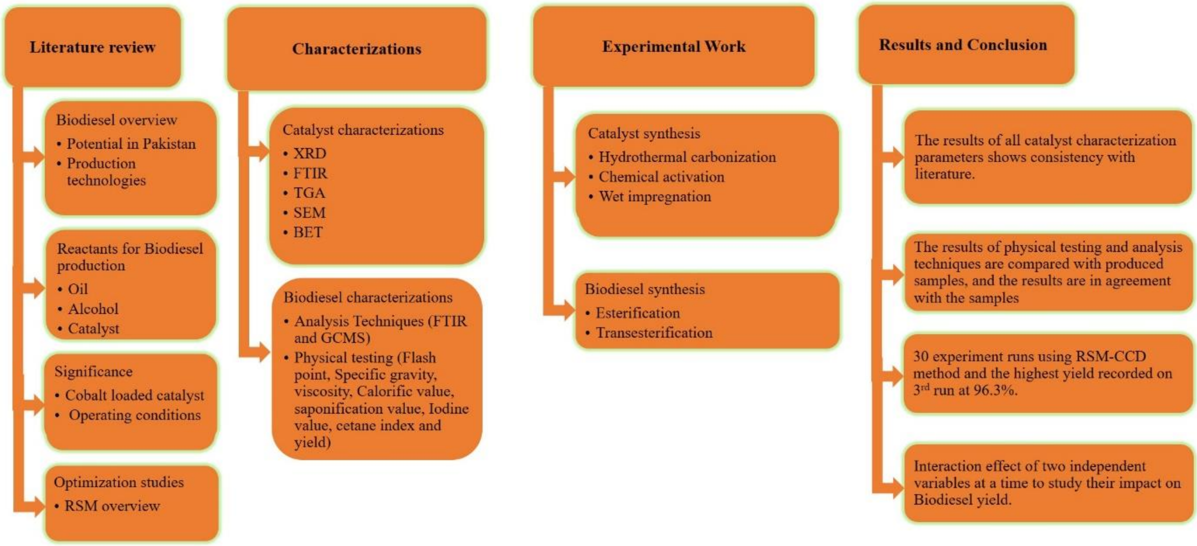

Fig. 1.2 Flow chart of the thesis

Summary

This chapter presents a succinct overview of the prevailing energy crisis in the nation, together with the concomitant environmental concerns stemming from the utilization of traditional fuels. A potential solution to this issue entails the utilization of sustainable sources of biodiesel, derived from sources such as previously consumed cooking oil. This measure presents a promising avenue to reduce the carbon footprint commonly associated with transportation reliant on nonrenewable fossil fuels. The present chapter expounds upon the process of producing biodiesel and elucidates the principle aim of the given research venture, namely to fabricate heterogeneous catalysts intended for application in the biodiesel synthesis procedure.

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Chapter 2 Literature Review

2.1 Biodiesel Overview

Even though the supply or production side does not appear to be very progressive or dependable, the concerns are necessary to strive for energy production from alternative renewable resources. Energy demand is expected to triple between now and 2050. The creation of second-generation biofuels employing non-edible plants, foods, and used vegetable oil as substrates is the focus of current research in the field of biodiesel manufacturing. To assist the cabinet's Economic Coordination Committee (ECC) in carrying out its decision to conduct research and development in this area, the GOP waived the tax and custom duty charges on the import of any utility required for biodiesel production, such as plant, machinery, equipment, and other items. To meet the aim of a 10% share by 2025, the Pakistan State Oil (PSO) company picked non-edible plant/seed species such as castor, Jatropha, and jojoba for biodiesel production. Pakistan's Alternative Energy Development Board (AEDB) has also begun biofuels efforts [1].

70% of Pakistan's population works in agriculture, and there are 79 distinct types of soil in total, making it a fertile region rich in natural species and agricultural justice. This is a practical element for bioenergy production since Pakistan has more than 80 million acres of poor-quality land appropriate for cultivating energy crops. Moreover, alcohol is required for the production of natural gas as well as biodiesel, which is readily generated from sugarcane. The greatest drawback of biodiesel technology as a potential source of renewable energy is a lack of knowledge, education, and institutional collaboration. Because they lack access to commercial energy, 60% of the rural population relies on traditional practices such as wood and organic waste (animal and agricultural residue) for household needs.

Because of energy crises and the steady rise in the price of fossil fuels, the globe is moving to renewable energy sources. Pakistan has struggled to satisfy its energy demands for many years. Most of the energy the world uses comes from oil. Instead of discarding the rice husk, it might be utilized to generate electricity. This would solve the problems of inappropriate garbage disposal and energy scarcity. Mirani et al. (2013) [2] discovered that Pakistan produces millions of tonnes of biomass annually. Rice is the most significant crop farmed in Pakistan. It is produced in around 1.78 million tonnes [3] with over 90% of it being burnt in the open air or thrown into rivers and lakes [4]. Rice husk may be produced in large quantities each year, and it is appealing for energy generation since it can be utilized in co-firing systems [5]. The majority of rice is produced in Pakistan, most notably in Punjab and the interior regions of Sindh. Every year, about 231,100 tonnes of rice husk are produced in Sindh, Pakistan [3, 6]. This husk is what remains after breaking the rice grain and accounts for 20% of the weight of rice [7]. The remainder may be used to fulfill the country's energy demands while also reducing environmental damage. According to Ali et al. (2016) [8] one tonne of rice paddy may generate 410-570 kWh of power from 220 kg of rice husk.

As a result, advancements in the field of bioenergy are required to considerably fulfill the nation's energy demands. As a result, progress in the field of bioenergy is required to considerably fulfill the nation's energy demands. Furthermore, sulfur oxide, nitrogen oxide, and particulate matter are among the 79% of highly toxic pollutants found in diesel emissions, which incorporate both natural and inorganic components that are infectious to both human well-being and the environment [9].

The major source of alcohol production from sugar cane is the nations around 21 distillery units, which can process over 2 million tonnes of molasses and create 400,000 tonnes of bioethanol, even if it exceeds the nation's additional exports by 318,000 tonnes. As a consequence, we have enough alcohol to finish the transesterification process required to generate biodiesel. Even though methanol is more commonly used for this operation because of its low cost. Pakistan can generate 56 million tonnes of biodiesel after cultivating all neighboring uncultivated land, but the country's present consumption is only approximately 8.5 million tonnes, even if an annual increase in energy demand of 10% is expected. Biodiesel has a potential future in Pakistan due to the availability of raw ingredients and particular energy generation projects [10].

2.2 Biodiesel production technologies

Both the economic and research worlds are experiencing rapid technological improvements in the biodiesel production process. The major barrier to biodiesel's adoption, however, continues to be its greater price as compared to petroleum-based fuel. To tackle this challenge, extensive research has been conducted in recent years to explore various techniques and technologies to enhance the financial and technical aspects of biodiesel manufacturing.

Diverse methods have been devised and applied to lessen the thickness of vegetable oils. These include using them directly or blending them, creating micro-emulsions, subjecting them to thermal cracking (pyrolysis), and carrying out transesterification [11-13].

2.2.1 Direct use and blending of Oils

Researchers have explored the possibility of replacing current fuels with vegetable oils ever since Rudolph Diesel, who invented the diesel engine, first used peanut oil as an alternative fuel in 1900 [14]. There are both disputes and restrictions associated with the use of vegetable oils in diesel engines. In recent decades, researchers have devoted a significant amount of effort to extensively explore a field that had been subject to experimentation for almost a century. An effective approach to overcome the issues related to the thick consistency of vegetable oils in compression ignition engines is to directly mix unrefined vegetable oils with diesel fuel or reduce their thickness by diluting them [15]. Research has indicated that the amount of energy utilized by pure vegetable oils is similar to that of diesel fuel [16]. Oil-to-diesel fuel ratios of 1:10-2:10 have shown short-term success [17]. Although some improvements have been made, it's still believed that using plant-based oils or mixtures of them in diesel engines, both direct and indirect, is not a good idea and won't work well [18]. Vegetable oils and blends can cause problems when used in diesel engines. These problems include thick oil, acid content, and carbon buildup. The oil can also form gums and create free fatty acids. This can make it harder for the engine to work properly [16]. When you heat and mix vegetable oils, they become less thick and can easily turn into gas. However, the basic structure of the oils stays the same and they still contain polyunsaturated fats [19]. Vegetable oils require considerable engine alterations, such as swapping out the materials used to build pipes and injectors. If the aforementioned condition is not fulfilled, the engine's operational duration will likely be curtailed, thereby subjecting the engine to greater wear and tear, subsequently leading to increased maintenance costs. Moreover, the risk of engine malfunction may also be exacerbated.

2.2.2 Micro-Emulsion of Oils

Micro-emulsification, commonly referred to as the generation of microemulsions by means of cosolvents, has been presented as a potential solution to address the issue of unduly high viscosity that is often observed in vegetable oils. Microemulsions refer to a type of colloidal equilibrium dispersion that exhibits optically isotropic fluid microstructures, possessing sizes that span within the range of 1 to 150 nm. The spontaneous emergence of microemulsions transpires as a result of the coexistence of two typically immiscible liquids and one or more amphiphiles, which may be either ionic or non-ionic in nature [16, 20]. Fuels based on micro-emulsions are sometimes referred to as "hybrid fuels". Nonetheless, it is noteworthy that mixtures comprising conventional diesel fuel and plant-derived oils have been commonly alluded to as hybrid fuels in scholarly discourse [21, 22]. Three elements make up microemulsions, which are transparent, stable, isotropic fluids made up of a surfactant, an oil phase, and an aqueous phase. The utilization of microemulsions containing solvents such as 1-butanol, ethanol, and methanol has been explored by scholars to achieve this goal. Various microemulsions, such as octanol, hexanol, and butanol, have demonstrated the propensity to fulfill the desired viscosity requirements of diesel engines [23]. A mixture of cetane improver, 2-octanol, methanol, and soybean oil in a proportion of 1.0:13.3:33.3:52.7 can generate a microemulsion. It has been demonstrated that this microemulsion has passed the 200-hour EMA (European Maritime Safety Agency) test [24]. The test found that adding a tiny amount of vegetable oil made the oil less sticky. This lasted for 200 hours in the lab test. But, it caused problems like injector needles getting stuck, lots of carbon building up, and not enough burning [17].

2.2.3 Pyrolysis of oils

Pyrolysis refers to a chemical reaction that leads to the transformation of an organic compound into a different form by exposure to elevated temperatures, either with or without the addition of a catalyst [25, 26]. Animal fat, vegetable oil, fatty acid methyl esters, and natural fatty acids are some examples of organic substances that can undergo pyrolysis to produce other chemicals [27]. The thermal cracking process represents a promising approach for the production of biodiesel from vegetable oils and animal fats, which are primarily composed of triglycerides. The methodology under consideration displays a marked resemblance to the typical procedures employed in conventional petroleum refining. Consequently, it exhibits significant potential in regions where hydroprocessing industries have already established a robust footing [28]. Numerous scholars have conducted investigations on the process of pyrolysis, involving the conversion of triglycerides, which yields liquid by-products exhibiting fuel characteristics analogous to those of diesel fuels. Two categories can be made from this study: methods that are catalytic and non-catalytic [28-31]. The complex structures and potential interactions of mixed triglycerides make the mechanisms for their thermal degradation expectedly complicated. The pyrolysis reactions of castor, palm, and soybean oils were investigated in a research study. By skillfully determining the distillation temperature (DT) limits, it was possible to produce fuels that possess the same physical and chemical characteristics as those demanded by petroleum-based fuels [29]. The capital investment required for thermal cracking and pyrolysis equipment is notably high, particularly for applications involving limited throughput rates. Moreover, while the final compounds bear chemical similarities to conventionally derived gasoline and diesel, the utilization of oxygenated fuel may nullify any ecological advantages via the process of oxygen depletion that occurs during thermal processing. This technique may occasionally produce more gasolene than diesel fuel and low-value byproducts [16].

2.2.4 Transesterification (alcoholysis)

Transesterification involves the conversion of triglycerides, like plant oils, through a series of chemical reactions with an alcohol (usually methanol or ethanol) and a catalyst (often sodium or potassium hydroxide). The result is the production of three molecules of fatty acid esters, also known as biodiesel, and one molecule of glycerol. This method is frequently employed in the manufacturing of biodiesel fuel using sustainable resources [32]. To improve the rate and efficiency of a reaction, a catalyst can be added. This process can also be reversed. To promote the manufacture of the intended item, an extra amount of alcohol could be incorporated. Various alcohols including ethanol, methanol, amyl alcohol, butanol, and propanol are employable in the process of transesterification. Ethanol and Methanol are extensively utilized owing to their affordability as well as their advantageous physical and chemical characteristics, including their polarity and having the briefest carbon chain. This technique yields a substance called fatty acid methyl ester (FAME), which can be used as a sustainable substitute for diesel fuel in engines [33]. The type of catalyst used, whether it is an acid or base (either homogeneous or heterogeneous), and lipase enzymes are among the factors that can impact the transesterification process. Several variables, such as the amount of catalyst present, the type of feedstock being used, the proportion of alcohol to oil, the rate of stirring, the temperature, the duration of the reaction, the quantity of unbound fatty acids, and the level of humidity, can all impact the process [34]. The process of transesterification includes combining the reactants while applying heat, and it can be reversed. Under the influence of heat, the reactants are combined to initiate transesterification, which is a reversible reaction. As illustrated in Fig. 2.1. Throughout the process of transesterification, a succession of 3 reversible reactions take place whereby a single mole of triglyceride interacts with 3 moles of alcohol, ultimately yielding one mole of glycerol and 3 moles of fatty acid alkyl ester. At every stage of the process, the triglycerides change to become diglycerides, which then progress into monoglycerides. As a consequence, a single alkyl ester molecule is produced. The process of transforming cottonseed, vegetable, and soybean oil into fatty acid methyl ester was carried out through the use of an alkaline catalyst, specifically sodium hydroxide by Keera et al. [35]. The researchers studied how different factors affected the transesterification process. The study examined the effects of varied reaction time (ranging from one to three hours), oil-to-methanol ratio (ranging from 1:3 to 1:9), and catalyst concentration (within the range of 0.5 to 1.5 weight to weight percent) on the explored system. According to the results obtained, the optimal conditions for achieving the highest percentage yield were comprised of a sodium hydroxide catalyst concentration of 1%, a methanol/oil molar ratio of 6:1, and a temperature of 60±1 °C for one hour. A method called "design of experiment" to turn useless shark liver oil into a helpful fuel called biodiesel was employed by Hatrooshi et al. [36]. They used two substances called sulfuric acid and sodium hydroxide to do this. Due to the high concentration of free fatty acids, the yield of FAME conversion using alkali-catalyzed transesterification was only 12% after 60 minutes, while acid-catalyzed transesterification achieved 40% conversion after only 15 minutes, indicating that alkali transesterification was less effective. The highest FAME conversion rate achieved by acid-catalyzed transesterification was 99%, using a methanol to oil ratio of 10.3 M, a reaction time of 6.5 hours, a temperature of 60°C, and a catalyst concentration of 5.9 wt% H_2SO_4.

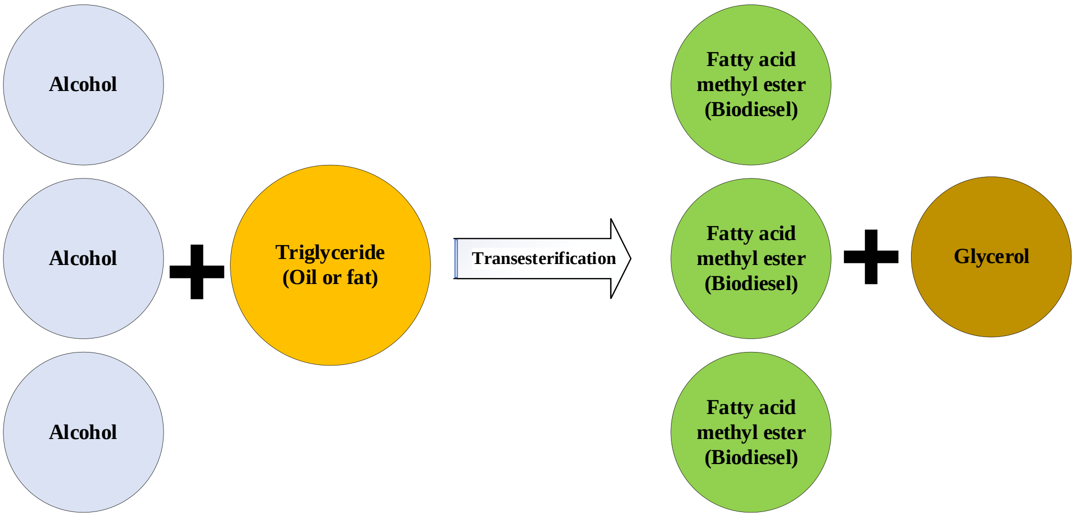

Fig. 2.1 Transesterification Reaction

2.3 Reactants for Biodiesel production

In the conventional process of producing biodiesel through the process of transesterification, the principal raw components utilized are either vegetable oil or animal fat, blended with alcohol, usually in the form of methanol or ethanol, and a catalytic agent. The confluence of the aforementioned reactants culminates in the synthesis of both biodiesel and glycerol. The ensuing explanation details the reactants involved in biodiesel production:

2.3.1 Oil

The presence of triglycerides within a diverse range of vegetable oils and animal fats is evident within the context of biodiesel production. The sources of oil may vary, ranging from commonly utilized substances like hog lard, cow tallow, canola oil, and soybean oil, to relatively less-known oils such as avocado or walnut oil. Biodiesel can be produced from utilized cooking oil or residual oil. Notwithstanding, the existence of contaminants like water, residue from meat, and breading engenders noteworthy challenges when transforming these oils into biodiesel [37]. Table 2.1 showcases a variety of research investigations that have delved into the creation of biodiesel using WCO as a base. Multiple research investigations have revealed that waste cooking oil can effectively act as a feedstock for biodiesel production, yielding up to 90%. This can be achieved by utilizing a variety of catalysts, encompassing both acidic and basic varieties.

Table 2.1 A WCO substrate for the production of biodiesel

Source of Oil	Catalyst	Reaction Temp (°C)	Oil to Alcohol ratio	Yield (%)	Conclusion	Ref
Food factory	NaOH	60	-	68-70	All five tested parameters complied with the ASTM criteria for fuel specifications.	[38]
Canola WCO	NaOH	60	1:3	94	Fourteen out of eighteen tested variables met the ASTM principles for fuel standards.	[39]
WCO	KOH	40	1: 6	99.5	The highest yield of 99.5 % under optimum conditions from both feedstocks.	[40]
Cottonseed WCO	Lipase	64	1:3	-	The optimum reactant ratio was 3, where the observed reaction rate was maximum.	[41]
WCO	NaOH	60	1:7	87	A conversion yield of 87% was achieved	[42]
WCO	NaOH	70	1:10	88.6	The density of the biodiesel product was high energy which could be compared with fossil fuel-based hydrocarbon.	[43]
WCO	BaO and KOH	80	1: 6	92	Less than 10% of energy is consumed during the microwave heating method than the traditionalone.	[44]
A mix of pig fat oil and WCO	NaOH	65	1:4	80	Optimized process parameters led to the maximum yield of 80 % by volume.	[45]
WCO	CZO	55	1:8	97.71	The catalyst due to its large surface area was reused for 5 cycles resulting in increased yield.	[46]
WCO	Ce-Mg/Al_2O_3	60	1:6	97	Ceria cobalt used less amount of catalyst than ceria magnesium to obtain more yield ofconversion due to its high surface area and fast activity.	[47]
WCO	KOH	66.5	1:6.18	92.76	The optimum condition of biodiesel production was obtained at 1 wt.% KOH.	[48]
WCO	HCl, H_2SO_4, H_3PO_4 KOH	50	1:2.5	94	Alkali catalyst for transesterification of WCO proved to be an efficient catalyst.	[49]

One of the most cost-effective and readily available options for producing biodiesel is to use WCO as feedstock. Finding a way to make biodiesel production financially viable can be difficult due to the expensive cost of feedstocks. However, using waste cooking oil as a source could be a practical solution to this challenge. Improperly getting rid of vast amounts of WCO in rivers and landfills leads to pollution. Therefore, utilizing WCO for producing biodiesel offers a much more environmentally friendly alternative to petrol and diesel. It also provides considerable advantages in terms of reducing pollution [50]. The transformation of used cooking oil into biofuel, which can serve as a replacement for traditional diesel, is imperative given the dwindling supply of oil reserves globally, environmental challenges linked to fossil fuel consumption, and the expensive cost of petroleum-based products worldwide. The utilization of unprocessed vegetable oils in compression ignition engines is faced with multiple obstacles due to the high thickness of the oils. The usual technique utilized for biodiesel production is transesterification, which is a chemical method that uses oil, alcohol, and a catalyst. Nevertheless, the utilization of WCO as a substrate presents a notable quantity of unbound fatty acids which necessitate the process of esterification before the transesterification stage. To expedite the reaction in the presence of alcohol, it is necessary to employ catalysts for both of these procedures. Generating biodiesel from waste cooking oil yields economic advantages and curbs environmental pollution stemming from the illegal discharge of copious quantities of this waste material into rivers and landfills [51].

2.3.2 Alcohol

One of the fundamental ingredients in biodiesel production is alcohol [27, 52]. Typically, an abundant amount of alcohol is utilized in the production of biodiesel to quickly achieve full conversion from oil [52, 53]. To transfer the reaction equilibrium towards the product's right side, alcohols are commonly used in transesterification. An alkali-catalyzed process can achieve a 98% conversion with a 6:1 alcohol-to-oil ratio. Overconsumption of alcohol raises the polarity of the solution, causing an increase in glycerol's solubility in the ester phase. As a result, the reaction between glycerol and ester turns around, leading to a reduction in ester production [54]. Different types of alcohol, such as methanol, ethanol, amyl alcohol, butanol, and propanol, are used in the production of biodiesel. The choice of alcohol can affect the efficiency of the transesterification process [27, 54, 55]. Normally, the transesterification process for producing biodiesel utilizes primarily ethanol and methanol alcohols, with their chosen application dependent upon their attributes and economic viability [56]. "Methanol is often the preferred alcohol choice for transesterification due to its desirable traits such as low viscosity, shorter reaction time, and a low molecular weight of 32.04g/mol. It is usually derived from mineral oil and is preferred over other alcohols for its superior performance [52, 54, 57-61]. Currently, methanol production relies on nonrenewable fossil fuels, such as natural gas.

It also exhibits poor immiscibility and solubility, leading to a mass transfer limitation [54]. The cost of methanol is subject to fluctuation based on crude oil prices, with prices ranging from $1.00 to $1.90 per gallon. To address this, researchers have explored alternatives to methanol, such as using methyl acetate as a substitute, which generates triacetin as a byproduct rather than glycerol. This approach typically involves the use of enzymes or supercritical conditions [62]. However, methyl acetate is not commonly used with natural or synthetic catalysts. Methanol remains the most common alcohol used in transesterification due to its suitability for the process [59].

Currently, 60% of global ethanol production comes from feedstock like sugar crops, making it a renewable alternative source [27, 60]. The production of ethanol from renewable sources through fermentation makes it a safer and less hazardous option [27]. However, ethanol's disadvantage lies in its lower reactivity of ethoxide when compared to methanol [54]. Moreover, separating and purifying ethyl ester from ethanol is more challenging, requiring greater effort and a longer reaction time. This difficulty in recovery makes the performance of ethyl ester inferior to that of methyl ester, resulting in decreased cost-effectiveness [27, 59]. The cost of ethanol varies depending on the source material used for its production, such as elephant grass, sugar cane, beer broth, or orange peels. The price range for ethanol is typically between $2.00 to $2.58 per gallon [63].

2.3.3 Catalyst

Considerable research has been conducted to develop catalytic materials that enhance the efficiency of various chemical reactions [64]. A substance that quickens the reaction rate of a chemical process without undergoing any depletion is known as a catalyst. It provides a surface for the reactants to interact and undergo activation. Heterogeneous catalysts are becoming increasingly popular due to their ability to be reused and their non-corrosive nature in conducting transesterification and esterification reactions, using both acids and bases. Several different kinds of catalysts have been developed including oxides of mixed metallics, metals, transition, and alkali-doped metals. Intelligently reworded: Agricultural waste, like rice husk, is an abundant and largely untapped by-product of rice milling. Its use as a catalyst could lower the expense of producing biodiesel when compared to traditional catalysts as shown in Table 2.2. This approach can also lower or even eliminate disposal costs and environmental impact, making it suitable for a numerous range of applications [64].

Table 2.2 Biodiesel production from Rice husk based catalyst

Feedstock	Catalyst	Findings	Yield	Ref
Palm Oil	RHS-KOH	The study focuses on investigating the catalytic behavior of rice husk silica produced via the impregnation method at various calcination temperatures.	94.39%	[65]
WCO	RHC/K_2O/Fe	The effectiveness of the separation process is primarily attributed to the exceptional magnetic characteristics of utilizing an external magnetic field, allowing for the successful recovery of the catalyst.	98.6%	[66]
WCO	RHS-CaO	The largest amount of CaO leaching mitigation was provided by silica support.	94%	[67]
-	RH-Biochar	The biochar made from rice husks using HTC can have additional uses such as purifying water and creating renewable energy.	-	[68]
WCO	RHC-SO_3H	The process of esterification and transesterification, which were previously done in two separate steps, have now been combined into a single step.	90%	[69]

Graphene oxide, silica gels, magnetite nanoparticles, resins, zeolites, and activated carbons are all efficient catalysts for the catalytic cracking process of WCO. Activated carbon is frequently implemented as a foundation due to its unstructured composition, which enables the formation of a remarkably permeable composition and an expansive measure of exterior space, reaching up to 3000 m^2g^{-1}. That's the reason behind its successful usage in the catalytic cracking process of WCO. An amorphous substance made up of carbon with highly developed micropores, derived from sources such as agricultural waste, wood, anthracite, and brown coal, is known as activated carbon. Since activated carbons are typically developed from high-carbon content-based organic matter, agricultural waste is an attractive option due to its low cost [70-72]. To produce activated carbons, the process involves two main stages. The initial stage involves carbonizing raw carbonaceous materials in an inert environment, followed by the subsequent stage of activating the product. The activation process can be of two sorts [73, 74], either physical using H_2O_2, steam, CO_2, or air [75, 76]; or chemical using NaOH, KOH, $ZnCl_2$, and so on, [71, 77, 78]. Chemical activation is a method that is often used because it needs less heat to work and produces more of what is wanted than physical activation [74, 79, 80].

Carbon materials made from waste [81], like carbon nanotubes (CN) and activated carbon (AC), are being used more often as catalysts in the process of catalytic cracking. This is because they have a big surface area and porous structure, which makes them work better [82]. It was shown that utilizing activated carbon increased WCO conversion and liquid product yield compared to the HZSM-5 catalyst [83]. During the catalytic cracking process of WCO, activated carbon exhibited a higher number of active reaction sites than MCM-41, which led to an expanded variety of liquid fuel products featuring reduced levels of oxygenated chemicals. This was the result of an enhanced deoxygenation process [84, 85]. In the context of catalytic cracking of WCO, a comparison was made between the effectiveness of various supports, including silica, alumina, zirconia, and activated carbon-supported MgO. Results indicated that the use of activated carbon-supported MgO as catalytic support resulted in significantly greater yields of C15 (8.1 wt.%) and C17 (10.2 wt.%) as compared to the other supports [86].

2.4 Significance of Cobalt-based catalyst for biodiesel productions

Metallic oxides are frequently utilized in catalytic processes to furnish the indispensable acidic and basic locations for the chemical reactions to transpire. These sites serve as active sites for reactant binding, thereby accelerating the reaction. It is generic to increase the efficiency of the catalyst by immobilizing and embedding the active metal phase onto a supportive substance characterized by extensive surface area and considerable porosity. This increases the likelihood of the reaction taking place by providing numerous accessible active sites for reactant binding. The support material also helps stabilize and prevent aggregation of the active metal phase, which can reduce its effectiveness. To put it concisely, catalyst reactions necessitate acid or basic locations which are provided by metal oxides. In addition, the active metal component is frequently linked to a very porous base with a sizeable surface area to enhance catalyst effectiveness [87].

The catalytic cracking of WCO is a significant method for producing liquid fuel products. Scientists have been exploring various catalysts to enhance the effectiveness of this technique [88, 89]. Recently, cobalt-based catalysts have become the focus of attention due to their enhanced catalytic performance in the cracking of WCO. Cobalt oxide, when affixed to highly porous supports like activated carbon, aids in decarboxylation and decarbonylation processes, which are crucial for synthesizing paraffinic and olefinic hydrocarbons. [90]. By utilizing activated carbon as a catalyst, cobalt was able to produce 91% hydrocarbons ranging in size from C8 to C20 through the deoxygenation process of palm fatty acid distillate. Additionally, there was a 72% preference for n-(C15 + C17) hydrocarbons [91]. Also, adding Co_3O_4 to the LaO_3/AC catalyst enhanced hydrocarbon output and n-(C15 + C17) selectivity. The Co_3O_4-La_2O_3/AC catalyst efficiently cracked WCO, resulting in a high yield of hydrocarbons spanning C8-C20, with a selectivity of 93% for n-(C15 + C17) and an overall yield of 96% [90]. As a result, cobalt-based catalysts offer significant promise for catalytic cracking of WCO for producing high-quality fuel range liquid products. Table 2.3 below depicts the use of cobalt-based catalysts in the synthesis of biodiesel. Furthermore, activated carbon support (RHAC) is derived from renewable resources such as rice husk, making it a more sustainable and eco-friendly choice as a support material compared to other materials that may be derived from non-renewable resources as shown in Table 2.3 below. Also, this study is distinguished by the use of WCO as a feedstock, which poses challenges due to its tendency to become rancid, but these issues were overcome during the esterification process. Despite this challenge, WCO offers benefits such as energy security, recyclability, and pollution reduction. Cobalt immobilization on Activated Carbon support (RHAC) shown in this study is a novel approach then other cobalt-containing composite material towards transesterification. Our study has advantages over others in efficiency, eco-sustainability, facile separation, and green pathway toward innovative catalyst synthesis. The use of transition metal catalysts, like cobalt, is important due to their ability to form strong bonds with oxygen atoms in ester groups of oil, facilitating transesterification reactions. Cobalt's easy immobilization on activated carbon (AC) makes it a convenient catalyst for biodiesel production, and its incorporation into RHAC enhances its catalytic performance, improving process efficiency. Furthermore, for heterogeneous catalysts, the ability to be reused is necessary. An intriguing fact is that the catalyst retained its action after being used three times. Productivity dipped after the fourth cycle, most likely because the active site leached to the surfaceCobalt-loaded AC has not yet been documented in biodiesel production.

Table 2.3 Relative catalytic performance using cobalt-modified catalysts for transesterification

Catalyst	**Oil used**	**Synthesis route**	**Operating Parameters**				**Conv.**	**Ref**
			Temp.	**M:O**	**Catalyst conc.**	**Time**		
Co-CaO	Microalgal biomass	Catalyst Prep.: Co-precipitation impregnation route Transesterification	65 °C	3:1	0.2%	120 min	98%	[92]
Co-ZnO	Mesua ferrea oil	Esterification/Transesterification	60 °C	9:1	2.5%	180 min	98.03%	[93]
Co/Fe mixed Oxides	Cooking oil	Transesterification (Catalyst Layered Doubled Hydroxides)	65 °C	6:1	2%	20 min	96%	[94]
MgCoAlLa–LDH	Canola oil	Ethanol Transesterification	100 °C	16:1	1%	300 min	95%	[95]
CoO-NiO promoted sulphated ZrO_2	Oleophilic oil	Cat. Prep.: Co-precipitation impregnation route Transesterification	65 °C	3:1	0.2%	120 min	98.80%	[96]

2.5 Significance of operating conditions in Biodiesel Production

Several operating parameters are verified throughout the process of producing biodiesel. The production of biodiesel is significantly impacted by four crucial factors: the proportion of alcohol to oil, reaction time, reaction temperature, and catalyst quantity. The efficiency and effectiveness of generating biodiesel depend significantly on these parameters.

2.5.1 Alcohol to oil ratio

The excess alcohol produced during the biodiesel reaction process correlates to the rapid conversion of oils and lipids into esters. The optimal molar ratio of alcohol to triglycerides (oil) must be cautiously monitored to guarantee the accomplishment of a thorough transesterification process. Theoretically, the stoichiometric ratio of one mole of methanol per one mole of free fatty acid (FFA) is needed for successful esterification. However, it has been observed that an excess of methanol results in augmented FFA transformation [49]. However, alcohol must be eliminated or recovered from biodiesel at a later stage for product purification [97, 98].

2.5.2 Reaction Time

The rate of ester conversion exhibits a direct correlation with the duration of the reaction period until an optimal time is reached. This optimal time may vary based on the properties of the substrate and catalyst utilized in the reaction. The reaction time is substantially influenced by the presence of reactants. The conversion efficiency of fatty acid esters has been observed to increase with prolonged reaction time [99], however, to get a high yield at a cheaper cost, the time duration must be adjusted [100]. The rate of esterification rises with time in general, but at a certain point, the activity stays constant regardless of time.

2.5.3 Reaction Temperature

As the temperature of the reaction increases, the viscosity of the oils decreases, thereby leading to an accelerated reaction rate over a shorter duration. It is necessary to decrease the temperature below the boiling point of alcohol. Moreover, after attaining an ideal temperature, further application of heat induces the process of saponification. The temperature dependence of the esterification process has been identified. Depending on the type of oil utilized, the temperature range that provides optimal performance was observed to fall within the range of 50-60 °C [101].

2.5.4 Catalyst Loading

Catalyst loading can have an impact on biodiesel yield. The rate of conversion of the substrate into biodiesel is directly proportional to the increase in catalyst concentration. Additionally, insufficient catalyst results in partial conversion of triglycerides to fatty acid esters. The ideal catalyst concentration for NaOH, the most often used catalyst, is around 1.5 wt.% [102]. Carbonates, hydroxides, and alkoxides classed as acids, alkalis, solid catalysts, and enzymes are among the catalytic components used in the transesterification process to manufacture around 10 million tonnes of biodiesel fuel from vegetable oil. Catalyst selection is primarily determined by the amount of FFA and raw materials in the oil; for example, oils with high water and FFA content will preferably undergo transesterification with acidic catalysts at high temperatures (60-100 °C) and longer reaction times (2-10 h) to avoid equipment corrosion [103]. Achieving the optimal concentration of an appropriate catalyst may be accomplished through the implementation of optimization techniques for a specific substrate. Alternatively, a potential outcome of the process is saponification or an incomplete chemical reaction.

2.6 Optimization of Biodiesel production

Specialized software tools, namely Mini Tab, Design-Expert Stat-Ease 6.0.8, and Design Expert 13, can be utilized for the optimization of biodiesel production yield through statistical analysis and design. Numerous methodologies, such as RSM, Factorial Design, Fractional Factorial Design, Crossed Design, and Mixed Design, are commonly employed to characterize and elucidate the production yield resulting from an experimental investigation. This approach can aid in achieving maximum efficiency in biodiesel production [104-106]. Two are explained below:

***Fractional factorial**:* The purpose of using this method is to evaluate the primary impact, interaction, and screening of multiple components to identify the significant ones. The factorial employed in this process can be of various types, such as irregular, universal, D-optimal, Plackett-Burman, or Taguchi OA, to achieve the desired outcome [105].

***Response surface methodology**:* The objective of this approach is to examine the influence of the reaction parameters on a given procedure, anticipate the optimum process conditions, and decrease the number of experimental attempts. To ascertain the aforementioned characteristics, an array of methodological approaches can be utilized, including central composite design (CCD), Box-Behnken, 3-level factorial, hybrid, one-factor, pentagonal, hexagonal, D-Optimal, distance-based, modified distance, user-defined, and historical data [104, 106]. The selection of these methodologies is contingent upon the particular necessities of the analysis at hand. The current investigation utilized RSM, coupled with a CCD, to analyze data and achieve optimal levels of purity and yield in biodiesel production. Moreover, the aforementioned methodology was employed to ascertain the factors that exert a substantial influence on the dependent variable. The selection of CCD in lieu of Box-Behnken was deemed advantageous due to its capacity to generate outcomes for numerous variables and facilitate the incorporation of more than three factorial magnitudes. On the contrary, the Box-Behnken methodology employs fewer than three factorial levels.

2.6.1 Response Surface Methodology (RSM)

RSM is widely utilized as a statistical analysis technique in optimizing biodiesel production due to its simplicity and linear function-based approach [106]. The primary objective of RSM is to analyze experimental data to understand the interaction effects among various process factors and construct a regression model to generate a 3-D response surface and contour map. This experimental design methodology is an effective way to quantify uncertainty and make inferences with a limited number of simulations. RSM can be broadly categorized into two types - CCD and Box-Behnken Design, which have distinct architectures. While working with RSM, selecting the appropriate experimental design that outlines the experiments to be conducted within the research region is crucial for the analysis [106].

CCD is a popular design tool within RSM that is commonly used to study and predict transesterification reaction parameters. It creates a quadratic surface that is excellent for process optimization and is good for carrying out sequential experiments. [107]. In the context of the experimental design known as central composite design (CCD), each factor is subjected to variation across five distinct levels. These levels include the axial point of plus and minus alpha, the factorial point of plus and minus one, as well as the central point. The placement of all the vertices on the surface is accomplished through the utilization of a sphere in charge-coupled device (CCD) technology. The CCD design is more intricate than the Box-Behnken design, as it lays out all the corner points on the surface, making it more detailed [108]. Omar et al. (2011) [105] employed the CCD technique to determine the optimal process conditions for FAME production by analyzing the interplay of process factors. The performance of the CaO catalyst was evaluated using RSM. The results of the full 24 factorial designs provided a robust prediction with a high confidence level of 95% using CCD. The RSM-CCD tool used by Jazei et al. (2013) [107] produced a quadratic polynomial model. Omar and Amin et al. (2011) [105, 109] engaged the services of RSM to conduct an analysis of the intricate interrelationships among the methanol-to-oil ratio, reaction temperature, reaction duration, catalyst loading, and free fatty acid (FFA) conversion that are central to the production of biodiesel from waste frying palm oil with the aid of Sr/ZrO_2 in the context of a CCD. Boey et al. (2011) employed CCD to conduct a statistical analysis of the use of mud crab shells as a catalyst in biodiesel synthesis. The present investigation revealed that the concentration of the methanol-to-oil molar ratio, catalyst, and reaction temperature were deemed as the most crucial variables influencing the yield of biodiesel production, ultimately leading to a yield of 93%. The selection of optimization parameters employed in the study was based on previous scholarly research, comprising time, catalyst loading, oil-to-methanol ratio, and temperature.

Summary

This chapter examines the viability of biodiesel as a sustainable energy source in Pakistan, providing an introductory assessment of the current state of biodiesel manufacturing worldwide, as well as in Pakistan, particularly with WCO. In this segment of the literature review, an assessment is made of the present status of catalyst synthesis for the production of biodiesel across the globe and in Pakistan. Notably, emphasis is given to cobalt-based catalysts employed for the biodiesel production process. As the supply of raw elements for the creation of biodiesel is restricted, attention is moving towards non-consumable origins. RSM is an effective approach that can be employed to optimize process parameters to amplify biodiesel output. To make the transesterification process economically feasible for commercial use, there is a need to create inexpensive heterogeneous catalysts that can be utilized in industrial environments as their high cost is currently restricting their use. Using biomass for energy is an eco-friendly and sustainable alternative that presents a great opportunity in the present landscape. Addressing the challenges that come with this option, it has been noted that transition metals possess qualities such as high catalytic activity and a large specific surface area, making them a promising area of focus in current research efforts.

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Chapter 3 Materials and Methods

3.1 Materials Preparation

Rice husk-based cobalt-loaded Activated Carbon (RHAC-Co) is synthesized by a three-stage method. This prepared catalyst falls in the category of heterogeneous solid catalyst. This catalyst has been used to perform transesterification of pre-treated waste cooking oil (WCO). Table 3.1 shows the list of feedstocks and chemicals used in this experiment.

Table 3.1 List of feedstock and chemicals used in this Experimentation

Sr #	**Name**	**Category**	**Purpose**
1.	Waste Cooking Oil	Feedstock	Triglyceride constituent used in transesterification
2.	Rice husk	Feedstock	The precursor used in catalyst synthesis
3.	Methanol	Chemical (99% pure)	Transesterification
4.	Sulfuric acid	Chemical (98% pure)	Esterification
5.	Potassium hydroxide	Chemical (85% Pure)	Activating agent
6.	Cobalt Nitrate hexahydrate	Chemical (99% Pure)	Impregnating agent
7.	Distilled water	99% Pure	Material synthesis and purification
8.	Deionized water	99% Pure	Material synthesis and purification

3.2 Catalyst synthesis

3.2.1 Mechanical Pre-treatment of Rice husk

In the pre-treatment process at first, the collected Rice husk (RH) was thoroughly rinsed with distilled water to remove contaminants and placed in an oven at 110 °C for 24 hrs to eliminate any residual moisture content (MC). The dried RH was ground to a particle size of 0.5-1mm using a microfine grinder (MF 10 BASIC) with a speed range of 300-650 rpm and a frequency of 50-60 Hz, then sieved through a fine mesh sieve to obtain a uniform particle size as shown in Fig. 3.1.

3.2.2 Hydro char production by Hydrothermal Carbonization

Crushed 10g of rice husk (RH) was added to 80 ml of deionized water and agitated at 750 rpm using a magnetic stirrer to achieve a homogenized mixture. The mixture was poured into a hydrothermal autoclave and then it was oven dried at 200 °C for 7 hours. The calculated mass yield of the prepared hydrochar (HC) was 60.5%. HC was rinsed with deionized water and filtered by grade 41 of Whatman filter paper. The resulting pH of the HC was 6.1 which is according to the literature range (5.0-7.5) [1] as shown in Fig. 3.1.

3.2.3 Chemical Activation of Hydro char

The dried hydrochar (HC) was chemically activated using 2g of HC impregnated with 1 M KOH solution and dried before processing in a tube furnace. Around 180 mL/min of nitrogen was pumped, and the tube was heated at 700 °C, ramp time of 5 °C/min of the furnace. The furnace was allowed to cool once the set point had been maintained for 2 hrs before the nitrogen feed was turned off. The pH of the activated carbon was neutralized using deionized water, followed by a wash with a 0.5 M HCL solution and oven-dried at 110 °C for 12 hrs. Ultimately, obtained product is rice husk-based Activated carbon (RHAC) as shown in Fig. 3.1.

3.2.4 Preparation of Metal loaded activated carbon

The wet impregnation technique was employed to achieve metal loading on RHAC. A 0.05 molar of an aqueous solution of $Co(NH_3)_2.6H_2O$ prepared, 5 wt.% of metal was loaded on the activated carbon. Then the resulting slurry was placed in a beaker with a stirrer and heated at 80 °C until all the liquid evaporated. The leftover powdered solution was oven dried at 110

°C for 24 hrs and calcined in the muffle furnace for 2 hr at 300 °C (to eliminate nitrates). Regarding the metal load, the prepared sample was labeled RHAC-Co as shown in Fig. 3.1.

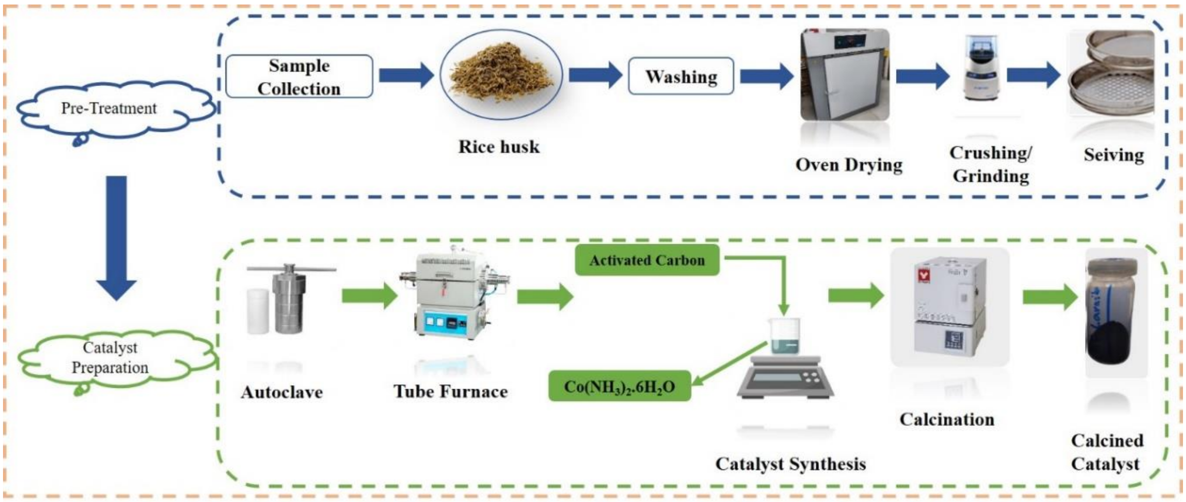

Fig. 3.1 Schematic representation of Co-loaded Rice Husk Activated Carbon

3.3 Catalyst Characterization

Research based on material synthesis highly requires characteristic analysis which is being done with the help of several characterization techniques available. This includes the examination of structure, elemental composition, and other chemical or physical properties which help in the accurate assessment of the sample to be used for the further application process.

The use of X-ray diffractometry (XRD) allows for the examination of various characteristics of a sample, such as its level of crystallinity, its purity, and its unit cell dimensions. This analysis was performed using Bruker's D8 Advance X-ray Diffractometer which features a Cu Kα radiation source at a wavelength of 1.5 Å and was connected to a computer interface for data analysis.

Fourier Transform-Infrared Spectroscopy (Cary 630 FTIR, Agilent Technologies, USA) reveals sample structural changes. Ge-ATR is a multireflection with ATR diamond crystal used. All samples' structural change was analyzed with Microlab expert software connected to the machine.

A Scanning Electron Microscopy (SEM) and Energy dispersive spectroscopy (EDS) study of RHAC-Co was performed using JSM-6490LA Analytical Low Vacuum SEM (SEMTech solutions, US).

Thermogravimetric analysis (TGA) was conducted to examine the thermal behavior of the catalyst samples using a SHIMADZU-DTG 60H instrument. The samples were subjected to temperature changes in a continuous nitrogen flow atmosphere (15 ml/min) from 20 °C to 800 °C.

Brunauer Emmett and Teller (BET) analysis measures surface area whilst BJH identifies pore diameter and volume. At 77.25 K, the micromeritics ASAP 2010 device measured surface area and pore volume.

3.4 Methodology for Biodiesel Production

3.4.1 Esterification

Esterification of WCO with 3wt. % Conc. H_2SO_4 as a catalyst decreased the acid value of the feedstock. The reaction was carried out at 55 °C for 3 hr with an oil-to-methanol ratio of 1:6 [2]. The acid value was monitored by sampling at regular intervals until it dropped to <1. After that, the synthesized catalyst RHAC-Co was applied to perform the transesterification of waste cooking oil (WCO) with a low acid value as shown in Fig. 3.2 (a).

3.4.2 Transesterification

Biodiesel production from WCO along with methanol and the loaded heterogeneous catalyst (RHAC-Co) was carried out on a laboratory scale. A 250-ml capacity flask is used to conduct the transesterification reaction. The flask was set up on a heating plate fitted with a magnetic stirrer and a temperature probe for precise control. Before adding methanol and catalyst to the reaction flask, WCO was preheated. The flask contained the calculated methanol-to-oil ratio. The mixture was then agitated for 10 mins with 1 to 3 wt.% of RHAC-Co catalyst for the mass of WCO. After adding 25 ml of WCO, the temperature of the mixture was varied from 60-90 °C at intervals of 5 °C. The transesterification proceeded for a time duration ranging from 45-60 min under 750 rpm (for all experiments) of continuous stirring. To perform as a standard and a base catalyst, commercial KOH was chosen to be combined with methanol before the esterified oil was added. On completion of the reactions, the catalyst and the glycerol layer were separated from the solution by centrifugation and methanol evaporation [3]. Synthesized biodiesel was examined as shown in Fig. 3.2 (b).

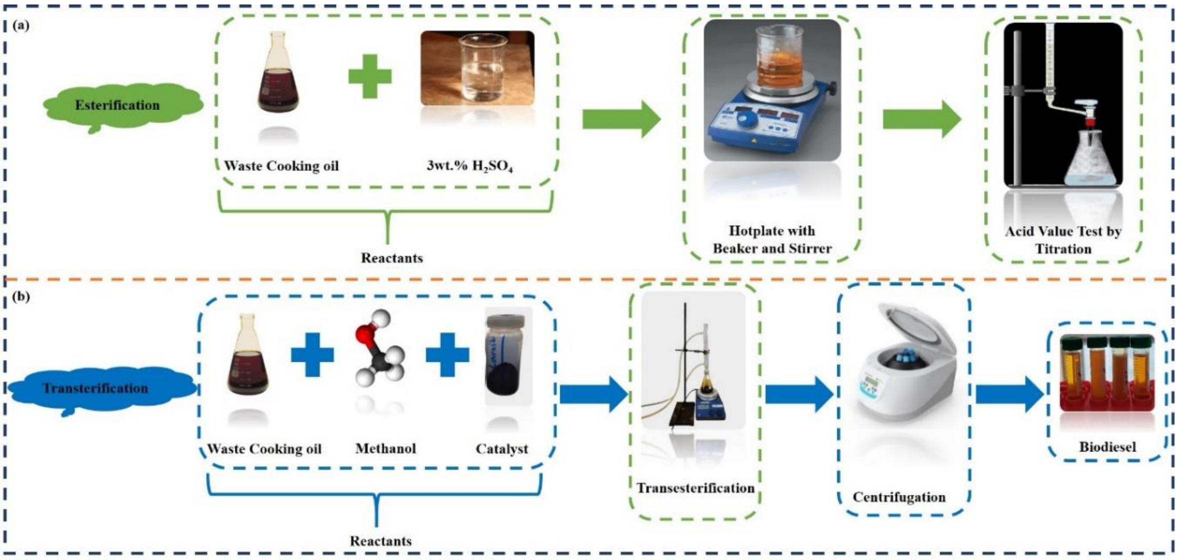

Fig. 3.2 Experiment setup's figurative representation of producing biodiesel in two steps via (a) esterification (b) transesterification

3.5 Optimization studies for the biodiesel yield by Response Surface Methodology (RSM)

The response surface approach was investigated for its potential to optimize and predict biodiesel yield. In the Design Expert-13 software, a CCD model was employed to study the independent variables (temp, (M:O) molar ratio, catalyst conc. %, and reaction time) effects on the prediction of the maximum biodiesel yield. This was done to make the most accurate prediction possible.

3.5.1 Experimental design

Design Expert-13 devised the experimental layout, and a testable mathematical model was created using Central Composite Design (CCD). Temperature (T), the methanol-to-oil molar ratio (M:O), the percentage of catalyst (%), and time (t) were outlined as the four independent factors for transesterification. Table 3.2 list these independent variables' ranges. Experiments were run with an M:O molar ratio between 1:6 to 1:12, with a reaction time between 45-60 mins, and with a catalyst concentration of between 1-3 wt.%. Within the context of Eq. 3.1, the term "system reaction" refers to the fraction of biodiesel volume to feed volume.

$$\text{Biodiesel yield} = \frac{\text{Volume of Biodiesel}}{\text{Volume of Feed}} \times 100 \qquad \text{(Eq. 3.1)}$$

The greater ranges and depths of the independent factors lend greater credibility to the CCD-based RSM approach. The RSM approach allows for the assessment of both the independent variable's effect and the interaction between factors. In addition, you may identify which parameters, or parameter combinations, significantly alter the system's reaction. Based on Eq. 3.2, we can get the required number of experiments (N) for a system with an (f) factor.

$$N = 2^f + 2f + C_o \qquad \text{(Eq. 3.2)}$$

Where C_0 equals central points. The response surface approach produces quadratic equation models.

Table 3.2 Independent variables' experimental range and levels.

Independent variables	Value	(Lower-upper)
Temp. (°C)	A	60-90
(M:O)	B	6-12
Catalyst Conc. (%)	C	1-3
Time (mins)	D	45-60

3.6 Biodiesel Characterization

Several biodiesel characterization techniques were used to assess if the synthesized biodiesel samples are lying in the standard range. The analysis techniques used here in this study are pH, specific gravity, density, viscosity, flashpoint, caloric value, GCMS, cetane number, iodine value, saponification value, and FTIR.

The Flashpoint of any material is the lowest temperature which indicates its flammability in the air hence the higher the flashpoint the safer and more easily storable the biodiesel sample is [4]. The biodiesel samples in the study were tested for flashpoint using Seta Flash Series 3 Active Cool Small Scale Flash Point Tester. The sample was fed into the inlet of the chamber where the flame was already lit with some gas supply.

The trend with which the biodiesel injection/supply affects the flame immediately at some specific temperature results in the flashpoint. The sample was tested at 80 °C, 110 °C, and 140 °C to reach the flashpoint of the sample.

The determination of the calorific value of a given specimen entails the complete combustion of a specified amount, whereby its quantitative representation is obtained in terms of joules per kilogram. The present inquiry aimed to examine the caloric content of the specimen under investigation through the employment of the 6200 Isoperibol Calorimeter. A sample of 0.5 g was initially weighed and introduced into the Oxygen Combustion Bomb with a temperature setting of 21°C. Subsequently, the temperature was incremented by 2°C for further analysis. The aforementioned procedure ascertained the calorific value of the specified specimen [5].

The FAME composition in the biodiesel specimen is ascertained via the employment of the Shimadzu GCMS-QP2020 NX gas chromatograph-mass spectrometer. To achieve this objective, 25 milligrams of the biodiesel specimen are dissolved in 0.5 milliliters of n-hexane, yielding a solution of the sample that is subsequently subjected to analysis via gas chromatography/mass spectrometry to identify and determine the composition of fatty acid methyl esters. The injection volume has been established at 1 μl, in conjunction with a split ratio of 20:1. Furthermore, the primary set temperature has been set at 150 °C, and a primary retention time of 5 minutes has been designated. The thermal processing conditions of the system involve subjecting the sample to a temperature of up to 220°C, with a gradual temperature increase of 10°C per minute, and an upper limit of 5 minutes for the retention time. The experimental protocol employed involved setting the inlet temperature and detector transfer line temperature to 250 °C and 300 °C, respectively. Additionally, the electron impact ion source mode was adjusted to 70 eV. The scan range in question has been established to span from 30-500 m/z. Furthermore, the ion source temperature has been set at 200°C, while the interface temperature has been established at 250°C.

The instrumental technique employed for analyzing the absorption spectra of the samples was the Cary 630 Fourier Transform Infrared (FTIR) Spectrometer. A minute quantity of specimen was deposited onto a glass slide and subsequently subjected to analysis through measurement of its spectral response across a range of wavelengths spanning from 650 to 4000 cm^{-1}.

The property of viscosity is defined as the measure of a fluid's inherent resistance to flow. The measurement of viscosity at ambient temperature (approximately 25 °C) for 2 ml of the sample at an angular velocity range of 50-150 rpm was conducted utilizing the Brookfield Ametek DV2T Viscometer.

The density of a substance can be defined as the ratio between its mass and volume. This measurement is typically expressed as mass per unit volume as in (Eq. 3.3).

$$\rho = \frac{m}{V} \qquad \text{(Eq. 3.3)}$$

To perform an estimation of density, the mass and volume of the sample were required to be determined. To achieve this, a designated quantity of the specimen was procured and weighed using precision measuring equipment [6]. The sample's glycerin content and fatty acid makeup affect the specific gravity value. This, denser vegetable oil processes into denser biodiesel which has high energy content and it results in increased power and better mileage. (Eq 3.3) was used to compute the specific gravity.

$$Specific\ Gravity = \frac{Density\ of\ Sample}{Density\ of\ Water} \qquad \text{(Eq. 3.3)}$$

The saponification value (SV), which is expressed in mg, is a calculation of how much KOH is needed to saponify a given volume of biodiesel. The saponification value is influenced by how the oil is subjected to pretreatment, as has been uncovered through research. To determine the saponification value, a mixture was created by combining 0.5 g of biodiesel with 20 ml of alcoholic (ethanol) KOH at a concentration of 0.5 N. The saponification reaction was completed when the mixture reached the desired clear solution after being heated and refluxed at 40 °C. The mixture was permitted to cool until the dissipation of the pink hue, at which point phenolphthalein was introduced as an indicator. Subsequently, the solution was subjected to titration employing 0.5 N hydrochloric acid. Using the relationship depicted in (Eq. 3.4), the saponification value was calculated.

$$SV = (\mathrm{B} - \mathrm{S}) \times N \times \left[\frac{56.1}{W}\right] \qquad \text{(Eq. 3.4)}$$

The variables denoted as S and B refer to the sample and blank values of hydrochloric acid, respectively. The variable N represents the normality of hydrochloric acid, while W denotes the weight of the biodiesel being analyzed [7].

The quantification of iodine uptake by 100 grams of oil is determined via the measurement of its iodine value (IV), which is denominated in grams. In this experimental procedure, a 0.1 g aliquot of biodiesel was amalgamated with 20 ml of carbon tetrachloride and 25 ml of Wijs reagent. The resultant mixture was vigorously stirred and subsequently allowed to stand in the absence of light for half an hour, to ascertain the iodine value. Subsequently, the reaction concoction was supplemented with 100 milliliters of distilled water and 20 milliliters of potassium iodide, having a concentration of 15%. The disappearance of the yellow color signaled the endpoint. Except for adding biodiesel, the same process was done for the blank, and the iodine value was determined using the equation presented in (Eq. 3.5).

$$IV = \frac{[(B-S) \times N \times 12.69]}{W} \qquad \text{(Eq. 3.5)}$$

In this formula, N represents the normality level of the $Na_2S_2O_3.5H_2O$ solution, while W is the amount of biodiesel being used. B stands for the volume in milliliters of 0.1 N $Na_2S_2O_3.5H_2O$ required for a blank test, and S represents the volume in milliliters required for the sample test.

The cetane number is a critical parameter used to assess the ignition quality of diesel fuel. It was computed using the equation shown in (Eq. 3.6)

$$Cetane\ Number = 46.3 = \left[\frac{5458}{SV}\right] - 0.255 \times IV \qquad \text{(Eq. 3.6)}$$

The product yield is the percentage quantity obtained at the end of the experiment in comparison to the number of reactants used for the biodiesel production process. This number tells about the extent of successful conversion of the substrate oil into biodiesel [7] as shown in (Eq. 3.7).

$$\text{Yield\%} = \left[\frac{Amount\ of\ biodiesel\ produced}{Amount\ of\ oil}\right] \times 100 \qquad \text{(Eq. 3.7)}$$

Summary

In this chapter, the experimental methodology employed to achieve the study's objectives is discussed. The first phase of the study involves synthesizing cobalt-loaded activated carbon using hydrothermal synthesis, chemical activation, and wet impregnation methodologies, respectively. The synthesized materials undergo characterization through a multitude of techniques, including TGA, BET, SEM, XRD, and FTIR, as elaborated upon in this chapter. The subsequent phase of the research entails the production of biodiesel via the processes of esterification and transesterification. The biodiesel samples obtained from the process were subjected to a range of analysis techniques to determine their specific characteristics. These included measuring the pH, specific gravity, density, viscosity, flashpoint, caloric value, GCMS, cetane number, iodine value, saponification value, and FTIR of the samples. The quality of the product is evaluated by comparing the results with the standard physical characteristics of biodiesel. Furthermore, an optimization setup for evaluating biodiesel yield is developed.

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Chapter 4 Results and Discussion

4.1 Characterization of the synthesized catalyst

4.1.1 Fourier transform infrared spectroscopy (FTIR)

FTIR is an analytical technique for the study of structural changes in chemical compositions, the determination of structural similarity between pure materials, and the investigation of structural changes in biomass as a result of thermal or chemical processing as shown in Fig. 4.1.

This research employed FTIR analysis to detect the functional groups present in four specimens (RH, RHC, RHAC, and RHAC-Co) and to determine if there were any alterations in the structural analysis following treatments like HTC, chemical activation, and wet impregnation. The study found a peak at 3200-3250 cm^{-1}, indicating an O-H stretch of alcohol was present in the samples due to the presence of moisture [1]. As thermal treatments were applied, this peak almost diminished. The Si-O-Si antisym stretch at 1100-1000 cm^{-1} was the most significant peak for all four samples since silica is the most crucial component in the rice material's chemical structure. However, it continued to be present with different temperature stages [2]. Another peak at 780 cm^{-1} shows the C=C bending and the peak at 1380 cm^{-1} indicates the presence of methylene group C-H in the developed catalyst (RHAC-Co) as a new entity after loading [3]. The Co–O peaks near 660 cm^{-1} implied that the RHAC-Co catalyst contained Cobalt [4], agreeing with the XRD results. This finding was also reported by Li et al [3] who used cobalt-loaded cherry biochar as a heterogeneous catalyst.

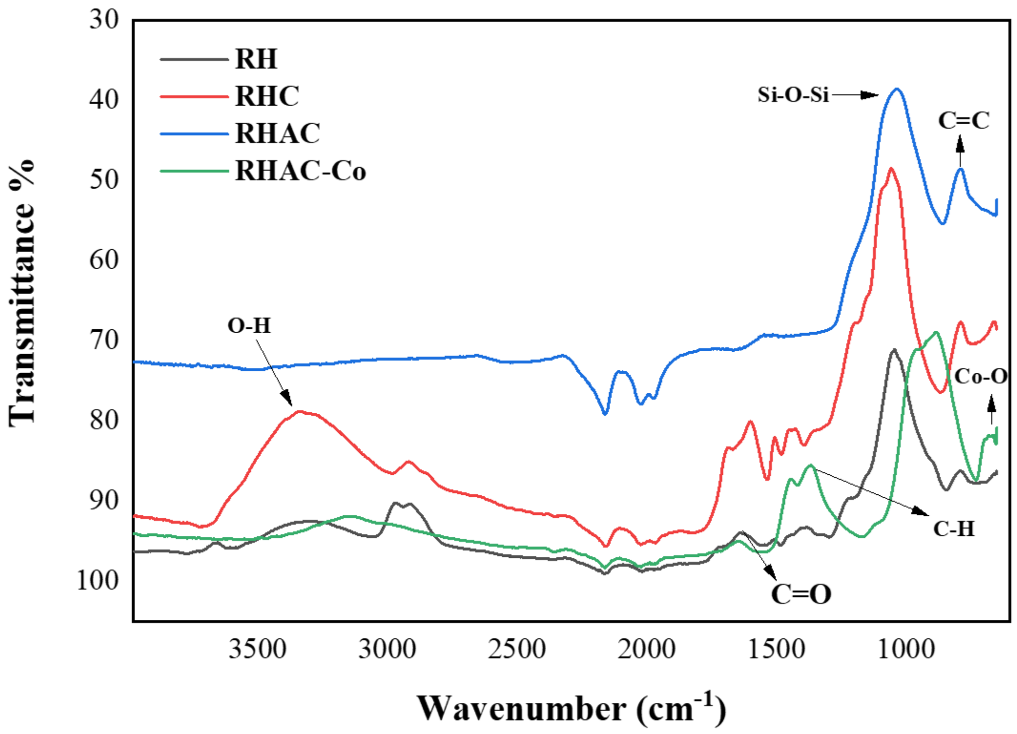


Fig. 4.1 Fourier transform infrared spectroscopy (FTIR) peaks of catalyst at various stages RH, RHC, RHAC, and RHAC-Co.

4.1.2 X-ray Diffraction (XRD) analysis

Fig. 4.2 represents the XRD profile of RHAC and RHAC-Co. The diffraction pattern of RHAC activated at 750 °C using KOH displayed broad diffraction peaks with no distinct peaks, indicating a primarily amorphous structure [5]. The RHAC sample featured two broad peaks around $2\theta = 26°$ and 43°, which can be attributed to reflection from the (100) and (002) planes [5, 6]. This is characteristic of amorphous carbon with disordered carbon rings, indicating a small degree of micro-crystallinity and a turbostratic graphite structure [7]. This supports preliminary studies by Nazzal et al. [8] which have reported that the broad peaks observed in AC samples are indicative of graphite-like micro-crystallites bound by a cross-linking network consisting of multiple graphite-like layers. The diffraction spectra of the RHAC-Co catalyst displayed discrete peaks of cobalt oxide crystallites at 26.5°, 31.5°, 36.82°, 59.5°, and 65.7°, similar to the previously reported study [9]. Furthermore, the absence of peaks from potential contaminants like nitrates in the RHAC and RHAC-Co samples, respectively, confirms the effectiveness of the washing process in achieving purity for the activated carbon and loaded catalyst [10].

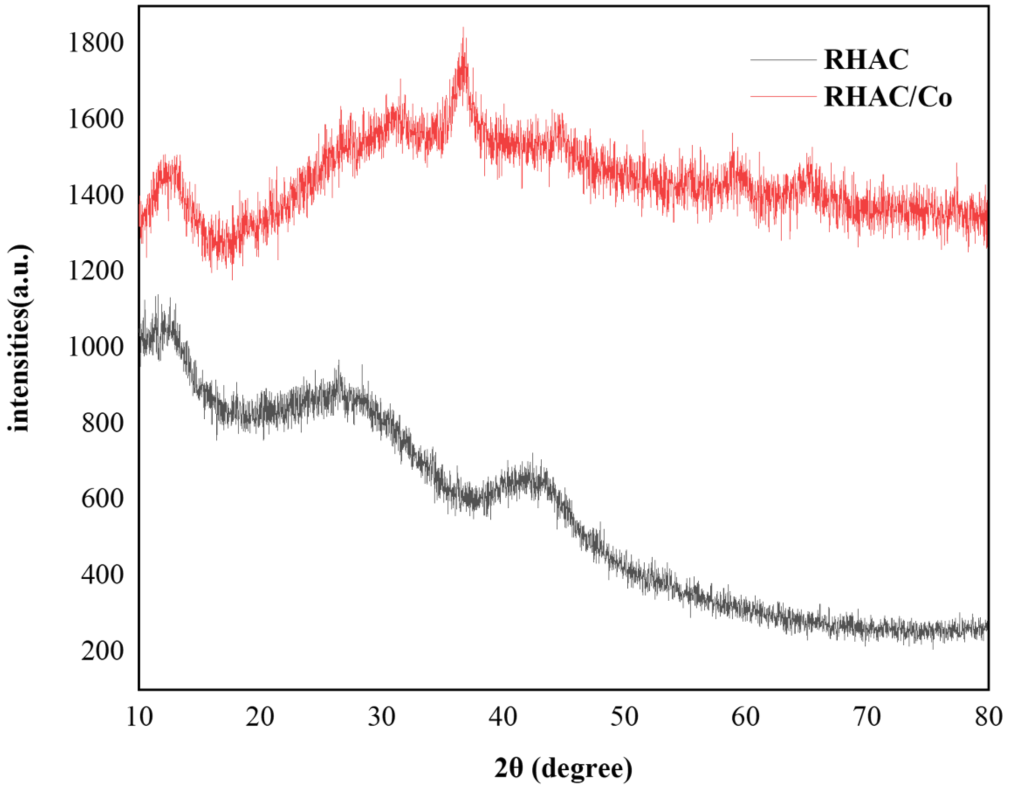


Fig. 4.2 X-ray diffraction (XRD) analysis of RHAC and RHAC-Co

4.1.3 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

SEM images of the RHAC and RHAC-Co are shown in Fig. 4.3 (a,b). The external surfaces of these RHACs reveal irregular large cavities, suggesting that the porosity of the material was created due to adding KOH reagent at 700 °C for activation. Pore development in the RHAC resulted in enhanced pore volume and surface area of the RHAC by promoting the dispersion of KOH molecules into the pores [5]. This microporosity could further help in the adsorbing characteristics of this material [11]. After the loading with the cobalt catalyst, the pores of RHAC were completely covered with the cobalt particles as shown in Fig. 4.3 (a). Fig. 4.3 (b) showed the presence of specks of cobalt oxides which depicted a brighter zone within the larger particles. The same bright specks were shown in the literature [9]. It was found that the cobalt oxide particles were well assimilated in the carbon samples. The Co-AC catalyst sample consisted of a partially agglomerated mixture of irregularly shaped small and large particles in terms of morphology and cobalt distribution. (non-uniform distributions) [12]. The elemental composition of RHAC-Co was verified by energy dispersive spectroscopy analysis (EDS) with a detector mounted on a microscope. The composition of RHAC-Co is made up of 56.5% carbon, 27.4% oxygen, 11.3% silicon, 2.3% cobalt, 0.1% potassium, 1.9% iron, and 0.5% calcium as shown in Fig. 4.4. By incorporating metal oxides, the catalyst is endowed with basic surface sites and a large surface area, greatly enhancing its performance in the transesterification reaction [13]. The potassium in the catalyst contributes to its high basicity and is responsible for its exceptional catalytic activity. Similar results have been observed in other heterogeneous solid base catalysts made from different biomass sources such as banana peel [14], tucumã peels [15], walnut shell [16], and Sesamum indicum [17].

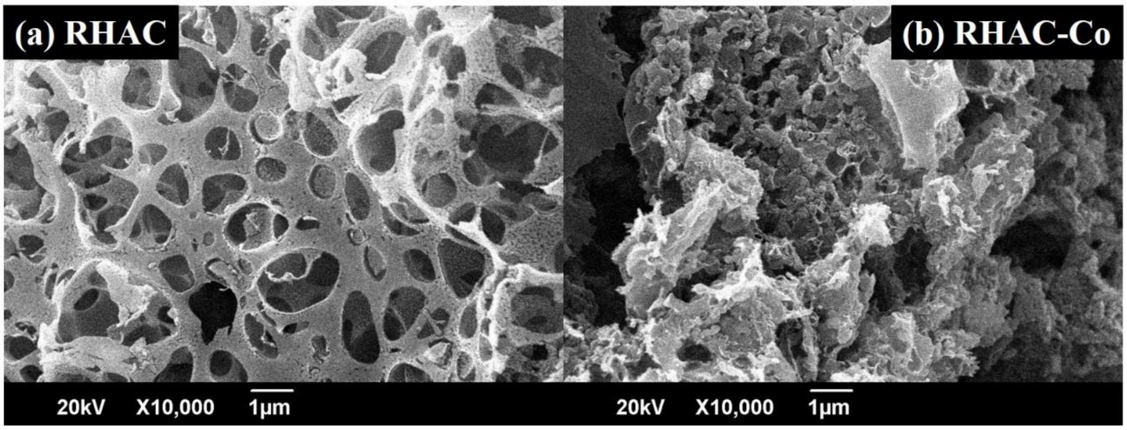
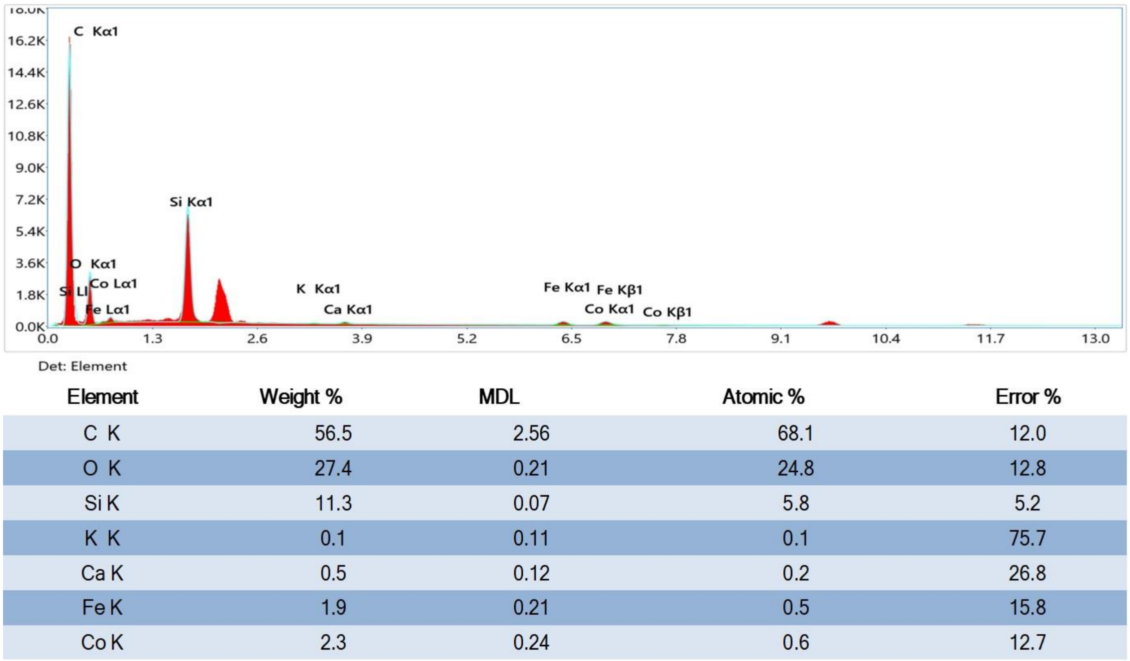


Fig. 4.3 Scanning Electron Microscopy (SEM) graphs (a)RHAC (b)RHAC-Co



Element	Weight %	MDL	Atomic %	Error %
C K	56.5	2.56	68.1	12.0
O K	27.4	0.21	24.8	12.8
Si K	11.3	0.07	5.8	5.2
K K	0.1	0.11	0.1	75.7
Ca K	0.5	0.12	0.2	26.8
Fe K	1.9	0.21	0.5	15.8
Co K	2.3	0.24	0.6	12.7

Fig. 4.4 Elemental composition of RHAC-Co by energy dispersive spectroscopy analysis (EDS)

4.1.4 Thermo-gravimetric analysis (TGA)

Fig. 4.5 shows the TGA analysis of the prepared RHAC before its loading with the metal to study the thermal stability. The thermal stability of the RHAC was compared with the RHC. It is clear from both samples that there is a minor loss before 80 °C, this is due to the elimination of moisture. The presence of moisture in the samples may have been absorbed from the environment during handling and storage. Up to approximately 300 °C, the samples remained relatively constant with only slight degradation. According to scientific consensus, this slight decomposition phase was likely a result of the breakdown of low molecular weight products. However, in RHC, an observable loss between 310-550 °C appeared. This occurred due to the breakdown of celluloses and hemicelluloses within the starting material (resulting in a 75% reduction in mass), resulting in the release of volatile substances [8, 18]. At temperatures as high as 600°C, the sample underwent a significant mass reduction, with just 18% of the original mass remaining. This indicates that the stable structural component lignin was broken down [5]. Moreover, RHAC's thermographic image displayed remarkable thermal endurance as it exhibited ultimate mean productivity of 69% despite being exposed to temperatures as high as 800 °C.

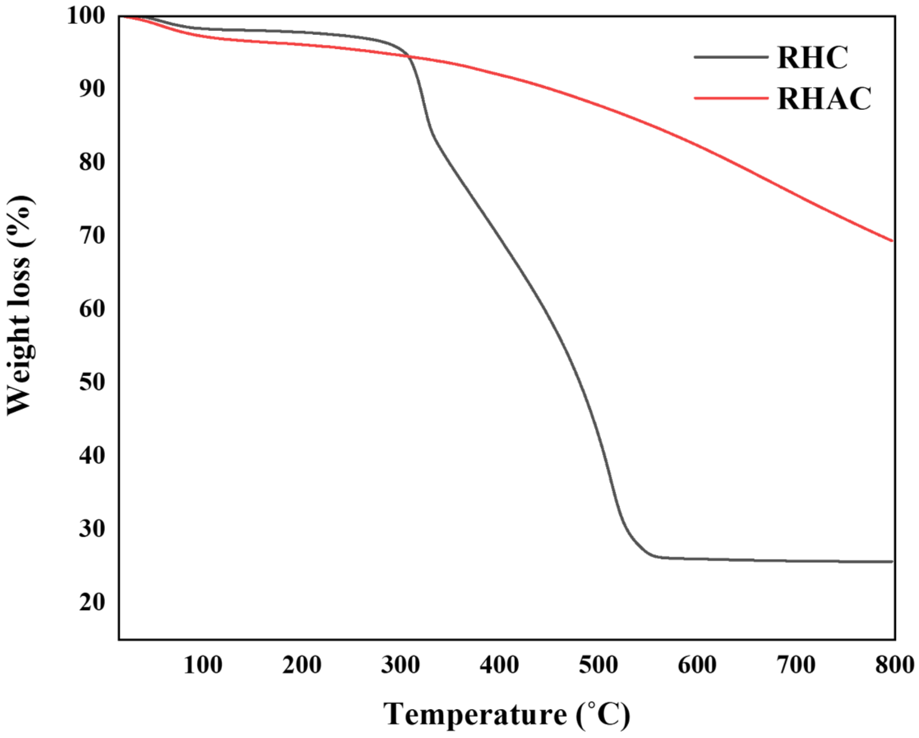


Fig. 4.5 Thermogravimetric analysis of RHC and RHAC

4.1.5 Brunauer-Emmett-Teller (BET)

An elevated BET surface area of 1219 m^2g^{-1} was observed by the RHAC used along with a microporous structure having a significant porous volume of 0.48 cm^3g^{-1}. However, the introduction of metal particles to the RHAC was anticipated to result in a decrease in the surface area [19]. Guo et al. [20] have demonstrated that lower surface areas in catalysts often indicate an increased concentration of basic sites present inside solid catalysts' interiors. This characteristic can aid in the transesterification process by facilitating the diffusion of glyceride into the interior of the catalyst [11] as shown in Table 4.1.

Table 4.1 BET analysis of RHAC and RHAC-Co

Type	**Surface area (m^2/g)**	**Pore size (Å)**	**Pore volume (m^2/cm^3)**
RHAC	1219.618 m^2/g	14.9	0.48
RHAC-Co	324.984 m^2/g	11.3	0.16

4.2 Biodiesel examination

4.2.1 Esterification

The analysis of the WCO revealed an elevated concentration of FFAs. To produce biodiesel, the FFAs must be less than 3%. Thus, a two-step transesterification reaction was selected as the solution. The optimal conditions for reducing the FFA content in WCO were determined to be a mixture of 60 ml of ethanol and 3% sulfuric acid, agitated at 55 °C for 3 hours at 300 rpm. This process successfully reduced the acid value from 7 ± 0.02 mg of KOH/g of oil to 3 ± 0.01 mg of KOH/g of oil.

4.2.2 Flashpoint of biodiesel

The flashpoint of RHAC/Co-BD was recorded at 140 °C, which is higher compared to conventional diesel and meets the standard requirement of 130 °C or above for biodiesel. This makes RHAC/Co-BD a safer alternative to conventional diesel [21]. The standard reference sample, KOH-BD, had a flashpoint of 130 °C. Biodiesel's specific gravity ranges from 0.86 to 0.90, with the standard reference sample KOH-BD having 0.9, and RHAC/Co-BD 0.88.

4.2.3 Specific gravity

The specific gravity of biodiesel is influenced by the composition of fatty acids and the presence of both free and bound glycerin. Biodiesel with a higher density provides greater energy and improves the mileage and power of engines. This is because denser vegetable oils tend to produce denser biodiesel since the specific gravity is determined by the concentration of fatty acids [22].

4.2.4 Calorific value

The calorific value, or energy content, of biofuels, is a significant characteristic for comparing their properties to that of conventional diesel fuel [23]. The low energy content may adversely affect critical performance indicators, such as torque and top horsepower [24]. Industry standards generally consider biodiesel to have a calorific value of around 37.27 MJ/kg. The energy density and calorific value of biodiesel can vary based on the type of feedstock used and the method of production applied. The calorific value of the RHAC/Co-BD was 40.07 MJ/kg while the standard reference sample KOH-BD had a calorific value of 46.05 MJ/kg.

4.2.5 Viscosity

The viscosity of biodiesel plays a role in both the combustion quality of the fuel-air mixture and the formation of biodiesel droplets. Both extremely low and high viscosity levels can negatively impact engine performance. When combustion is inefficient, black smoke may be produced as a result of poor viscosity and lack of penetration. Additionally, if the fuel is too viscous, it may have difficulty flowing through the injector and could potentially freeze the cylinder wall, reducing the amount of fuel that is burned [25]. For KOH-BD and RHAC/Co-BD, the WCO biodiesel was found to have a viscosity of 3.74 and 5.72 mm^2/s, respectively. This is a normal value, falling between the ranges of 1.9 and 6.0 mm/s (ASTM D6751-02, 2002).

4.2.6 Density

Engine performance is substantially impacted by the density of biodiesel. To ensure efficient combustion in the engine, the density of the biodiesel must be within a specific range to achieve the optimal air-fuel mixture High-density diesel is unacceptable because it can result in incomplete combustion and the release of particulates, however, this issue can be resolved by blending conventional diesel with biodiesel. Diesel has a standard density of 848 kg/m^3, while biodiesel ranges from 870-900 kg/m^3 [21]. Higher than conventional diesel fuel, biodiesel has a density of about 0.88 g/cm^3 (870 kg/m^3- 900 kg/m^3). Calculated density for WCO biodiesel showed that RHAC/Co-BD had a density of 899 kg/cm^3, which is consistent with the fuel standard (ASTM standard).

4.2.7 Iodine Number

Biodiesel's degree of unsaturation can be quantified by measuring its iodine number; this provides valuable insight into the oil's stability. Fuel polymerization occurs when unsaturation levels are high because epoxides are formed when oxygen is added to double bonds [26]. Biodiesel should have an iodine number of 120 g I_2/100 g oil. The iodine content of KOH-BD, the standard sample, was 57.5 g I_2/100 g, while that of RHAC/Co-BD was 61.32 g I_2/100 g.

4.2.8 Saponification value/ FFA content

If the saponification value of biodiesel surpasses 312 mg KOH g^{-1} of oil, soap production may occur, reducing yield and product quality. In comparison to the ASTM 6751 standard, the saponification values of the synthesized biodiesel were lower, with RHAC/Co-BD demonstrating the least value at 193.4 mg KOH g^{-1}.

4.2.9 Cetane number

The cetane number of biodiesel is determined by the carbon number of the fuel and the concentration of FAME. The ideal range for biodiesel is between 46 and 52, while for conventional diesel, it's 40 to 55. Reference sample KOH-BD had a cetane number of 50.5, while RHAC/Co-BD had 51. The synthesized biodiesel is better since the samples have the right FAME and carbon numbers.

4.2.10 Product yield

The choice of substrate, catalyst, and other reaction factors greatly affect how much biodiesel is produced with the amount of substrate utilized [25]. Because of this, the outcomes of product yield alter when these reactants and reaction circumstances change. The product yield after performing transesterification reactions using both synthesized catalysts was 96.3% for (RHAC/Co-BD) and 98% for (KOH-BD) standard catalyst. Table 4.2 depicts the outcomes of an optimization-based analysis performed using RSM on the RHAC/Co-BD sample, which aimed to gauge the influence of different independent factors on the ultimate yield.

Table 4.2 Comparison of Physicochemical Characteristics between RHAC/Co-BD and KOH-BD as the Standard.

Properties	**Unit**	**BD standards**	**BD from WCO (ASTM 6751) Ref.[27]**	**KOH- BD**	**RHAC/Co-BD**
Flashpoint	°C	>130	130	130	140
Specific gravity	————	0.86–0.9	0.8743	0.9	0.9
Viscosity	**mm^2/s**	1.9–6.0	5.83	3.74	5.72
Calorific value	**MJ/kg**	>35	37.2	46.048	40.068
Saponification value	**mg KOH/g**	<312	280	112.2	252.45
Iodine value	**g I^2/100g oil**	<120	63.5	57.5	60
Cetane number	**----**	≥47	51.48	50.5	51
Yield	**%**	94	98	78.33	96.3

4.2.11 Fourier Transform Infrared Spectroscopy (FTIR)

The biodiesel's Fourier-transform infrared (FTIR) spectra reveal the presence of the alkene and alkane C-H bonds within the wave number range of 1400-1500 cm^{-1} and 2800-3000 cm^{-1}, respectively. The graphical representation, designated as Fig. 4.6, is commonly used in academic writing to visually illustrate and supplement the author's points and arguments. Such illustrations and figures can greatly enhance the reader's comprehension and engagement with the presented content. The spectral data in Fig. 4.6 suggests the existence of an oxygen moiety, specifically, the C-O bond within the spectral range of 1000-1300 cm^{-1}. Additionally, the ester C=O bond within the range of 1735-1750 cm^{-1} was detected, alongside the bending vibration of $(CH_2)n$ at 723.27 cm^{-1}. In contrast to traditional diesel fuel, the current iteration of biodiesel exhibits significantly lower levels of environmental pollutants and facilitates thorough combustion through its incorporation of oxygen. These XRD results match the findings from prior studies in the literature [28, 29]. The biodiesel produced from different catalysts, such as KOH-BD and RHAC/Co-BD, showed the same functional group peaks of C-H and C-O bonds as shown in the respective Fig. 4.6.

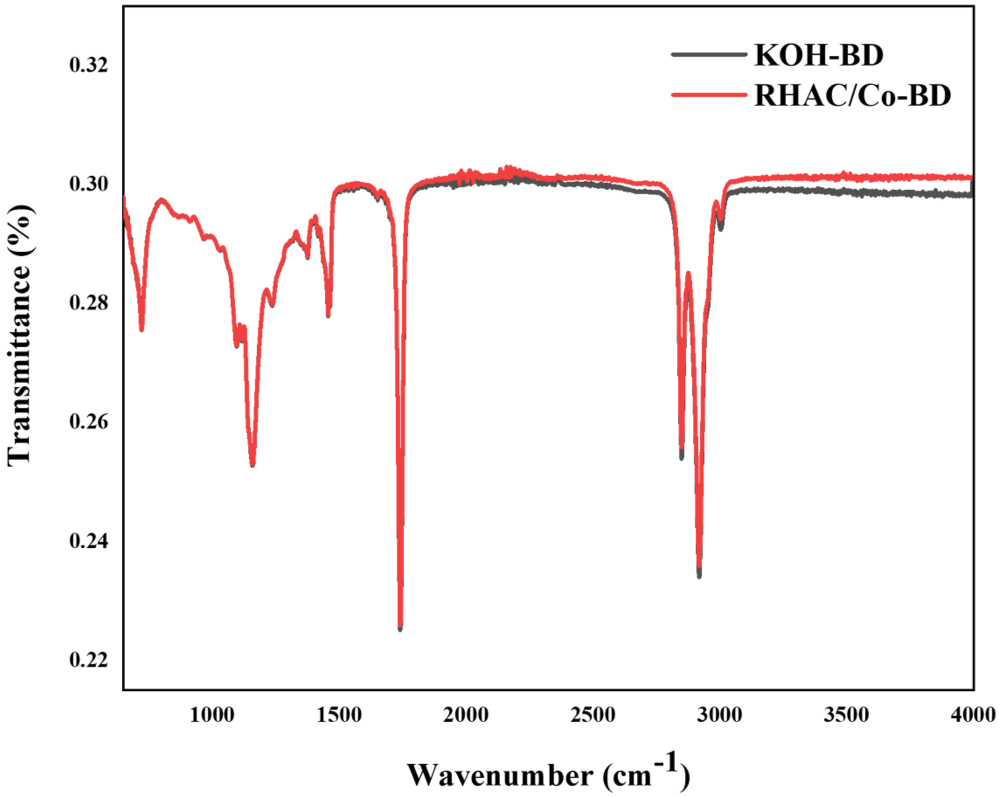


Fig. 4.6 Fourier transform infrared spectroscopy of RHAC/Co-BD and conventional KOH-BD.

4.2.12 Gas Chromatography-Mass Spectroscopy (GC-MS)

Fig. 4.7 and Table 4.3 display the retention period and fragmentation pattern data from GC analysis, which reveals six primary distinctive FAME peaks. The composition of FAME and their commonly used names in the production of biodiesel, with special emphasis on identifying the optimal conditions required for this process, are determined. However, the GC analysis shows that the highest possible biodiesel mass yield was 96.3%. The percentage of FAME present was roughly 93.89% by weight, while the efficiency of conversion reached 90.38%.

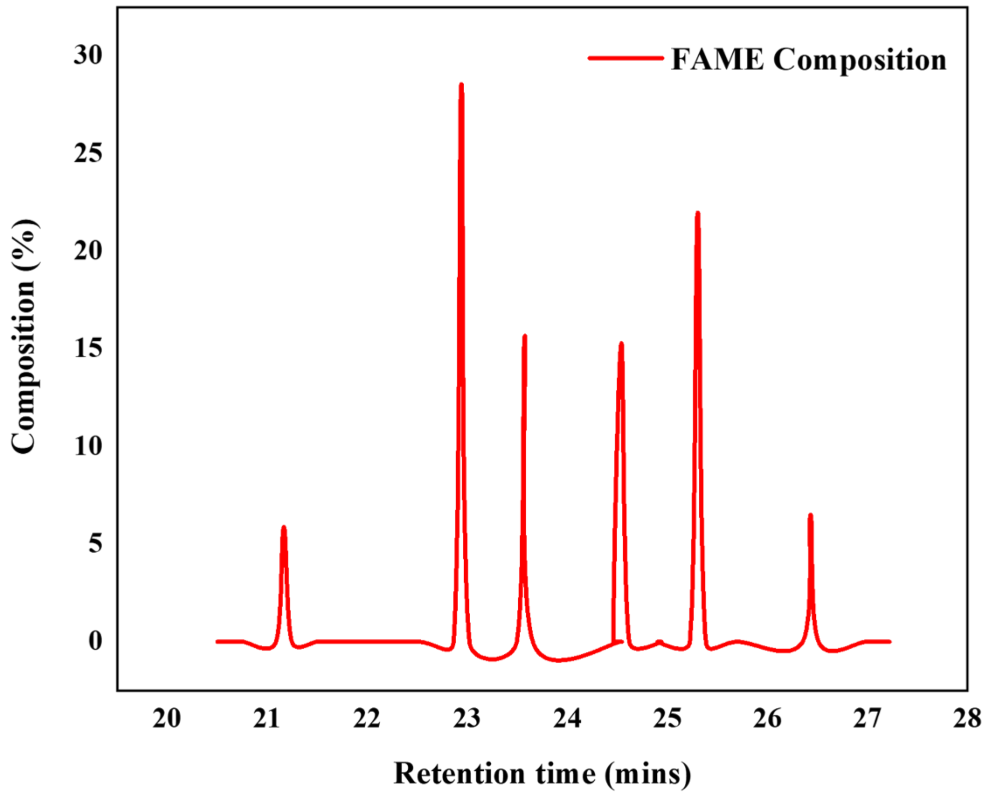


Fig. 4.7 Fatty Acid Methyl Ester (FAME) peaks

Table 4.3 Fatty acid methyl ester content present in RHAC/Co-BD

Peaks	Fatty Acid Methyl Ester	Common Name	Formula	Retention Time (min)	Composition (%)
1.	Hexadecanoic acid methyl ester	Methyl Palmitate	$C_{18}H_{36}O_2$	22.942	28.56
2.	Octadecanoic acid methyl ester	Methyl Stearate	$C_{18}H_{36}O_2$	25.305	21.98
3.	*cis*-9-Octadecenoic acid methyl ester	Methyl Oleate	$C_{18}H_{34}O_2$	24.540	15.30
4.	cis-9-cis-12-Octadecadienoic acid methyl ester	Methyl Linoleate	$C_{18}H_{32}O_2$	23.575	15.67
5.	cis-9,12,15-octadecatrienoic acid	Methyl linolinate	$C_{18}H_{30}O$	26.432	6.50
6.	Pentadecanoic acid, 14-methyl-, methyl ester	Methyl pentanoate	$C_{17}H_{34}O_2$	21.167	5.88

4.3 Optimization Studies performed for biodiesel yield by Response Surface Methodology (RSM)

As shown in Table 4.4, 30 experiments using the CCD method were conducted and their respective biodiesel yields were recorded. The results reveal that the maximum biodiesel yield is achieved in the 3rd run at 96.3%. To ensure the accuracy of the results, various figures were analyzed, including a graph comparing predicted and actual values, as shown in Fig. 4.8. A close correlation between observed data and RSM predictions is indicated by the clustering of points close to the line y=x. To validate the results of the RSM, an Analysis of Variance (ANOVA) was conducted. Table 4.5 of the ANOVA findings show that model terms A, C, D, AB, AC, CD, A^2, B^2, C^2, and D^2 are significant (their P-values are less than 0.0500), while model terms with P-values more than 0.1000 are not significant. R^2 and R^2 adj, which highlight the importance of the Quadratic model, were also calculated to ascertain the model's precision. By comparing actual and predicted values, we find that the model provides a high level of accuracy for estimating process yield ($R^2 = 0.9723$). Table 4.6 displays the estimated RSM optimum values for the factors, with a maximum output of 96.3%. The RSM's prediction was checked by doing the trials twice under ideal conditions, where both times the average value was found to be 96.3%. Therefore, the optimal settings found can be applied in practice with little or no error.

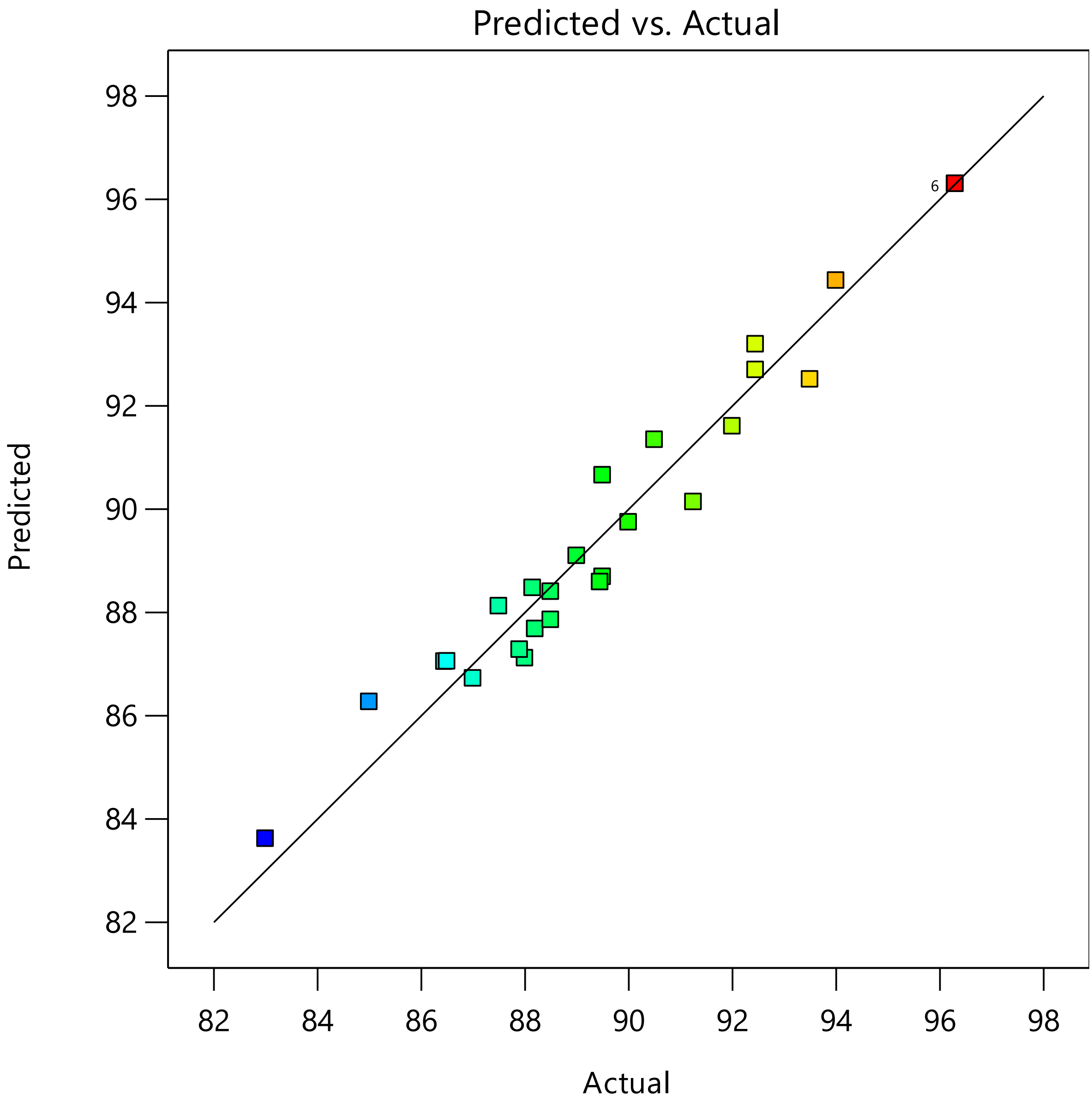


Fig. 4.8 Comparing the actual-predicted deviation

Table 4.4 CCD matrix with four independent variables and experimental response

Runs	Factor 1 A: Temp. °C	Factor 2 B: M:O mol/mol	Factor 3 C: Catalyst Conc. %	Factor 4 D: Time (min)	Response 1 Yield %
1	90	6	1	60	87.9
2	75	15	2	52.5	94
3	75	9	2	52.5	96.3
4	60	12	3	45	88
5	90	6	3	45	92
6	75	9	2	52.5	96.5
7	60	12	1	45	89
8	75	9	2	67.5	88.5
9	60	6	1	45	88.2
10	60	12	1	60	91.25
11	75	9	4	52.5	86.5
12	90	12	3	60	93.5
13	60	6	1	60	86.45
14	90	12	1	45	88.5
15	75	3	2	52.5	92.45
16	90	6	1	45	89.5
17	75	9	2	52.5	96.3
18	105	9	2	52.5	90.5
19	90	6	3	60	92.45
20	60	12	3	60	89.5
21	75	9	0	52.5	83
22	75	9	2	52.5	96.3
23	45	9	2	52.5	88.15
24	75	9	2	52.5	96.3
25	90	12	1	60	87.5
26	60	6	3	45	87
27	60	6	3	60	89.45
28	90	12	3	45	90
29	75	9	2	52.5	96.3
30	75	9	2	37.5	85

Table 4.5 ANOVA for biodiesel yield

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	413.31	14	29.52	37.65	< 0.0001	significant
A-Temp.	12.33	1	12.33	15.72	0.0012	
B-M:O	2.28	1	2.28	2.91	0.1087	
C-Catalyst Conc.	17.68	1	17.68	22.55	0.0003	
D-Time	6.83	1	6.83	8.71	0.0099	
AB	5.06	1	5.06	6.46	0.0226	
AC	15.02	1	15.02	19.15	0.0005	
AD	0.6006	1	0.6006	0.766	0.3953	
BC	1.05	1	1.05	1.34	0.2652	
BD	2.81	1	2.81	3.58	0.078	
CD	6.25	1	6.25	7.97	0.0128	
A^2	74.49	1	74.49	94.99	< 0.0001	
B^2	12.42	1	12.42	15.84	0.0012	
C^2	213.76	1	213.76	272.62	< 0.0001	
D^2	144.05	1	144.05	183.71	< 0.0001	
Residual	11.76	15	0.7841			
Lack of Fit	11.76	10	1.18			
Pure Error	0	5	0			
Cor Total	425.07	29				
	R^2=0.9723	-	R^2_{adj}=0.9465			

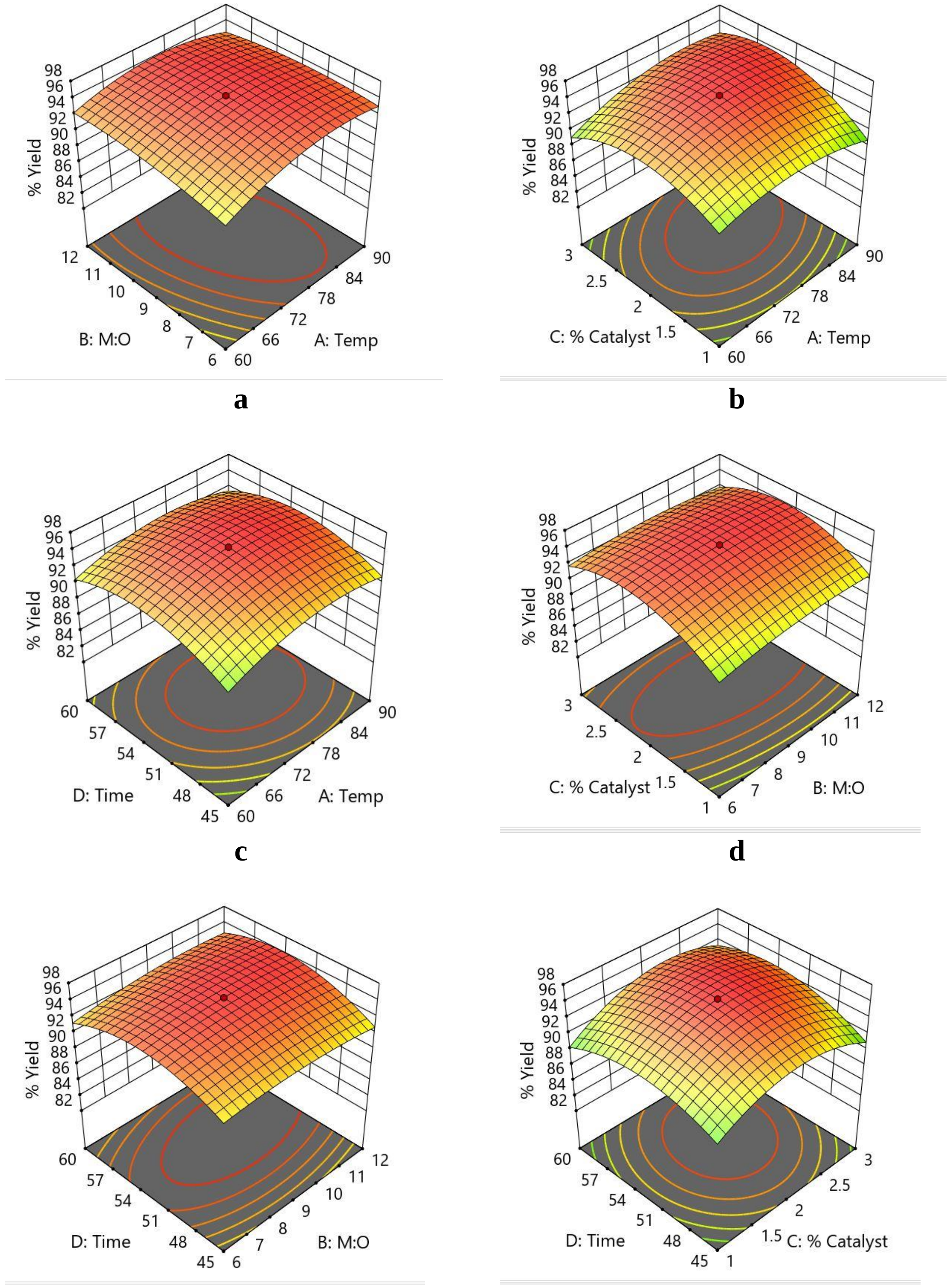
Table 4.6 Optimum result yielded by Resource Surface Methodology

Item	**Temp.** °C	**M:O** mol/mol	**Catalyst Conc. %**	**Time** min	**Yield** %
Value	75	9	2	52.5	96.3

4.4 Interaction effect of independent variables for yield studies

To analyze the independent variables, three-dimensional figures are utilized, and their impacts on biodiesel are studied by comparing two factors at a time while the remaining two factors are at optimum. This is done so that the optimal conditions can be justified. Given in Fig. 4.9.

Fig. 4.9(a) demonstrates yield response to temperature and M:O variables at the optimal time and catalyst concentration. As could be observed, the biodiesel yield was slightly lower at 60 °C compared to 75 °C, and when this temperature was held at 60 °C and 75 °C the biodiesel yield increased with an increase in the M:O ratio but as the M:O ratio reached about 12:1 there was a sharp drop in the yield at both temperatures. The reason could be that the higher quantity of methanol might have increased the glycerin solubility in the reaction mixture causing a reverse glycerolysis reaction to occur [30].



a b c d e f

Fig. 4.9 3D response surface plots for comparison (a) Temperature (A) vs methanol to oil ratio (B) (b) Temperature (A) vs catalyst (C) (c) Temperature (A) vs time (D) (d) M:O (B) vs catalyst (C) (e) M:O (B) vs Time (D) (f) Catalyst (C) vs time (D)

Fig. 4.9(b) demonstrates yield response to temperature and catalyst conc. variables at the optimum time and M:O ratio. With an increment in temperature from 60 °C to 75 °C, the yield increased with an increase in the catalyst conc., but at concentrations more than 2 wt% catalyst roughly, the yield dropped dramatically due to soap formation and lower conversion from triglyceride to FAME [31]. By comparing Fig. 10(a) and Fig. 10(b), it is clear that when temperatures are above 60 °C, the impact on the yield is similar for the catalyst concentration and the M:O ratio.

Fig. 4.9(c) demonstrates yield response to temperature and time variables at optimum catalyst conc. and M:O molar ratio. At 60 °C, the layer of biodiesel was not clear (viscous), also the density was higher from glycerol so to tackle that, the temperature was raised to 75 °C which gave the highest yield of 96.3%. So, it's clear that up to 75 °C, the effect of temperature is more important than that of reaction time. However, the increase in temperature decreases the retention time from 60 to 52.4 mins while giving the highest yield. Likewise, a previous Study found that high temperatures enhanced the reaction by reducing retention time. The phases separated at around 0.5 hr at higher temperatures compared to 0.25 hr at lower temperatures [31].

Fig. 4.9(d) demonstrates the yield response to M:O and catalyst conc. variables at optimum time and temperature. A higher concentration of catalyst (more than 1.8%) and a higher molar ratio of M:O (greater than 8.5) result in the highest yield. Here, the heterogeneous catalytic process required a somewhat larger M:O molar ratio. Excess methanol over the optimum ratio has been shown in several studies to reduce yield by reducing the amount of catalyst that comes into contact with the oil [32]. Developing the oil-alcohol interface requires increasing both the methanol concentration and the catalyst concentration. The reaction kinetics consequently improves with an increase in the interface [33].

The effect of M:O ratio vs time on yield at optimum catalyst conc. and temperature is demonstrated in Fig. 4.9(e). That suggests that going from an M:O ratio of 8.5 to 9.0 boosts yield by a factor of 1.5 when the reaction time is increased from 45-52.5 min. It is possible to claim that when reaction time increases, the rate of conversion of FAME also increases. Owing to the initial mixing and dispersal of the alcohol into the oil, the reaction starts slowly. The reaction speeds up steadily and rapidly with time. At 50 min, the yield is at its highest and remains roughly stable with additional increases in reaction time. Based on this data, it appears that a response time of 48–53 min is optimal. However, if the reaction period exceeds 60 min, the product yield will decrease due to the reverse reaction of transesterification, which will cause esters to be lost and more fatty acids to form soaps. A higher molar ratio for a given time boosts methyl ester synthesis, as reported in a previous study. Considering the same rationale, the findings of that study yielded an equivalent yield of 94.9%, while in my instance it was 96.3% [34].

Fig. 4.9(f) illustrates biodiesel yield response to time and catalyst concentration. At the optimal temperature, the catalyst's effect on yield was examined between 1-3 wt.% under 45-60 min reaction periods. Biodiesel yielded 96.3% at 2wt% catalyst. For a 3wt% catalyst, increasing concentration gradually decreased yield by 87%. This indicates soap production due to extra catalyst and slower triglyceride to FAME conversion, which reduced biodiesel yield. 52.4 min with 2 wt.% catalysts yielded the most biodiesel. A heterogeneous catalyst made from pyrolyzed rice straw and sulfonated was compared in an earlier literature search. Transesterification yielded 97% biodiesel in approximately 6 hrs [35]. In this study, the catalyst cuts time by 85%.

Summary

This chapter presents the characteristic analysis of the synthesized RHAC-Co. The results obtained from FTIR, SEM, XRD, and TGA are compared with previous studies, and the findings are validated by the literature. The biodiesel samples produced using the synthesized catalysts are also compared with the standard values, and the results fall within the specified range. XRD, SEM, and TGA are used to characterize the synthesized catalysts, and the analysis results agree with the literature review. The XRD results indicate broad amorphous characteristic peaks of AC, while the RHAC-Co catalyst shows distinct peaks of cobalt oxide crystallites. The SEM images show cubical images of 1μm for both RHAC and RHAC-Co, while the TGA results demonstrate excellent thermal behavior of RHAC-Co.

The synthesized catalysts are then utilized for the preparation of biodiesel production, and two separate reactions are performed for both catalysts to produce biodiesel samples. Various standard testing and analysis techniques are employed to compare the produced samples, and the results are in agreement with the samples. The flashpoint of RHAC/Co-BD is 140 °C, and the calorific value is 40 kJ/g.

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Chapter 5 Conclusions and Recommendations

5.1 Conclusions

In conclusion, a new solid transition metal loaded biomass-derived heterogeneous catalyst called RHAC-Co was prepared that showed great catalytic activity towards transesterification and was characterized using XRD, FTIR, SEM-EDS, TGA, and BET. Rice husk-derived activated carbon (RHAC) was used as a support material due to its sustainability, high surface area, porosity, and thermal stability. The addition of transition metal cobalt to RHAC resulted in a composite RHAC-Co with superior catalytic activity to RHAC. These properties make it an attractive support material for the loaded catalyst RHAC-Co. The green catalyst is justified by the analysis. The catalytic activity of the composite RHAC-Co was found to be superior to that of RHAC, likely due to the presence of active basic sites and cobalt metal. SEM-EDS analysis confirmed the presence of these elements Co, K, and Ca in the catalyst, which likely aided in the transesterification process. BET analysis also revealed that the addition of transition metal cobalt caused a reduction in the surface area from 1219 m^2/g of RHAC to 324.984 m^2/g of RHAC-Co and pore volume from 0.48 of RHAC to 0.16 m^2/cm^3 of RHAC-Co suggesting that a decrease in surface area can lead to an increase in the concentration of basic sites within the catalyst and further promotes the transesterification process. The loaded catalyst was effectively used in the transesterification of waste cooking oil (WCO) and methanol, achieving a maximum biodiesel yield of 96.3%, in line with ASTM standards. Response surface methodology (RSM) was used to optimize the reaction parameters and showed that it is a good tool for yield optimization by studying the interrelation between independent variables. This study highlights the potential of using waste-derived products as substrates for sustainable biodiesel synthesis and emphasizes the use of transition metal loading to aid in transesterification.

5.2 Recommendations

- One recommendation for producing biodiesel is to utilize waste materials and green pathways, rather than synthetic catalysts.

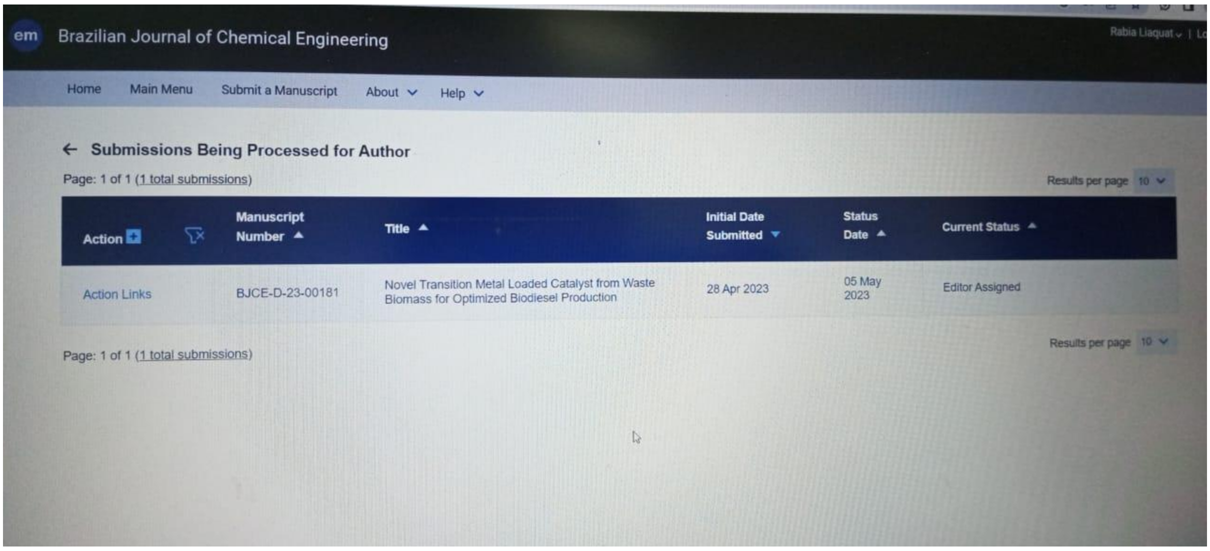
- Waste materials that can be used in biodiesel production include animal fats, cooking oils, and other organic materials that would otherwise be discarded. This can have several benefits, including reducing waste and pollution and reducing dependence on non-renewable resources.

- On a commercial scale, several aspects need to be considered. First, the availability and cost of the waste materials or other feedstocks must be evaluated to ensure a reliable and cost-effective supply. Second, the efficiency and scalability of the green pathway must be tested to ensure that it can meet the demand of large-scale production.

Appendix-A

“Novel Transition Metal Loaded Catalyst from Waste Biomass for Optimized Biodiesel Production.” ***Laraib Aamir Khan[1], Rabia Liaquat[1,*], Muhammad Usman Khan[1], Abdul Basit[1]***

Brazilian Journal of Chemical Engineering (Under Review) (IF = 1.772)



Submissions Being Processed for Author

Page: 1 of 1 (1 total submissions)

Action	Manuscript Number	Title	Initial Date Submitted	Status Date	Current Status
Action Links	BJCE-D-23-00181	Novel Transition Metal Loaded Catalyst from Waste Biomass for Optimized Biodiesel Production	28 Apr 2023	05 May 2023	Editor Assigned

Page: 1 of 1 (1 total submissions)