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Silica extracted from ragihusk as heterogeneous catalyst for synthesis of biodiesel from waste cooking oil

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Abstract:

Each year an estimated 1.3 billion tons of agricultural waste are produced worldwide, with staple crop residue forming a large bulk of the generated waste. This crop residue from cereal crops like Ragi husk is generally discarded despite being a rich silica source and is a widely used compound with an ever-increasing demand. In the present project, the process of extracting silica from agricultural waste has been studied, and the optimal conditions for the extraction of silica were reported. The extracted silica was used as a catalytic support for KOH and employed for the synthesis of biodiesel. The structural, morphological, and elemental characterizations of the silica sample were done using X-ray diffraction (XRD), DTA-TGA analysis, and Fourier transform infrared spectroscopy (FTIR). Scanning Electron Microscope (SEM) And Energy-Dispersive X-Ray Spectroscopy Analysis (EDS/EDX). The XRD study showed the presence of amorphous silica in the Ragi husk sample. The DTA curve for the Ragi husk silica sample indicated two distinct stages: all organic matter was decomposed in the first stage. The characteristic bands resulted from FTIR analysis were indicative of the presence of pure silica. SEM and EDS analysis also indicated the presence of high-purity silica. The physio-chemical characteristics of the catalyst were studied using XRD, TGA, and FTIR. The transesterification of reactants (waste cooking oil and methanol) was performed using a KOH-impregnated heterogeneous catalyst at reaction conditions with mole ratio 6:1, catalyst loading 3 w/w%, temperature 65 °C resulted in 83% yield of biodiesel. The present work proposes an economical pathway to valorize agricultural solid waste effectively.

Keywords: Heterogeneous catalyst; Ragi husk; Silica; Transesterification; Waste cooking oil

1. Introduction

The agricultural sector is one of the most indispensable parts of the global economy, employing over one billion people worldwide and contributing to upwards of 20% of GDP in developing nations. Each year, several million tonnes of crops are produced for consumption, ranging from cereals to fruit and vegetables. Cereal crops are the most widely grown staples, with wheat and rice accounting for over 50% of total cereal production. Due to the large-scale agricultural production, a large amount of byproduct or agricultural waste is generated. An estimated 1.3 billion tons of agricultural waste is generated each year globally. This waste, known as process residue, can be utilized by farmers as fertilizer cattle fodder or processed and used as soil enrichment. However, many farmers generally burn these residues in the open air, leading to global warming, pollution, and the hastening of ozone layer hole formation. Two significant components of agricultural waste burning are the incineration of husks and straws of various crops[1]. Cereal crops are monocots, and the process residues of many monocotyledonous plants have a high percentage of silica present in their cell walls, some having as high as 10% dry weight basis of silica content[2]. Silica is an abundantly available and highly versatile mineral and is used in an extensive range of applications. Crystalline silica finds application in the making of refractory bricks[3], thermal insulation, ceramic manufacture and in the making of concrete. Amorphous silica, on the other hand, has a much wider range of applications, from making laboratory glass [4] and adsorbents to its use in zeolites and in the pulp industry[5]. Traditionally, silica is most commonly extracted from quartz sand or industrial sand. This sand is reacted with sodium carbonate powder at high temperatures, resulting in the formation of Sodium silicate, which is further treated with acids such as Sulfuric Acid to precipitate Silica [6]. However, due to the rapidly depleting quartz sand resources, alternatives have been suggested and considered. Multiple methods have been studied and reported in the literature regarding the production of silica, such as reverse microemulsion[7], a hydrothermal method [8], and flame synthesis from tetraethoxysilane[9]. Most of these methods involve the use of highly toxic and expensive precursors such as tetraethoxysilane.

Due to the rapid increase in world population, industrialization and commercialization have raised the global energy demand. Consequently, this causes a decrease in the availability of fossil fuels and an increase in world health problems [10]. In light of their finite availability and detrimental effects on the environment, it is necessary to reassess the usage of fossil fuels. Renewable and sustainable energy sources are gaining popularity to meet energy demand [11]. As a result, alternative green technologies that are more sustainable must be developed. Biodiesel can be produced in more significant quantities using vegetable oils and animal fats as a sustainable alternative[12].Given that it originates from living plants and animals; it is regarded as a form of renewable energy. It is often used to power engines for vehicles, notably those in airplanes. It can replace fossil fuels like petroleum-derived diesel [13].

Ragi husks, an unwanted by-product of Ragi cultivation, are used as fuel in boilers, resulting in the production of large amounts of silica-rich ash. Finger millet husk, or Ragi husk, has seen only a little research and study as a potential source of silica but has been shown to contain reasonable quantities of extractable silica in its straw and husk, the obtained silica is lightweight, has a vast external surface area and is highly porous [14] as it is monocotyledonous in nature and is widely grown in various regions of India. Most extraction routes from agricultural biomass revolve around the production of ash between 500-900°C, with 700°C being the ideal temperature for the product to be amorphous in nature and possess desirable properties like a large surface area and high purity. A study showed that the amorphous silica content of the optimum Ragi Husk Ash sample was noted as being 95.00% when burnt at 700°C after three hours of pre-treatment, while multiple studies show that pre-treatment with HCl gives a very high purity of amorphous silica obtained [15].

The present work focuses on silica extraction from agricultural waste like Ragihusk, which is utilized as catalyst support for biodiesel synthesis. The procedure for the extraction of silica from agriculture has been presented in detail. The characterization of the extracted silica was done using various techniques using Scanning Electron Microscope (SEM), X-Ray Diffraction, Thermogravimetry, Energy-Dispersive X-Ray Spectroscopy Analysis (EDS/EDX), and Fourier Transform Infra-Red (FTIR). The characterization revealed that the silica obtained is in good agreement with the commercial-grade silica. This process can be utilized to extract silica from agricultural waste continuously. The KOH impregnated on the extracted silica proved to be the better heterogeneous catalyst for the synthesis of biodiesel.

2. Materials and methods

2.1 Materials

The Ragi husk utilized in the present study was collected from the local fields in Karnataka, India. The chemicals used, Hydrochloric acid (HCl, 37%), Potassium Hydroxide (KOH, 97%) and Methanol were purchased from Sigma-Aldrich, India. Deionized water (DI) was utilized to prepare the solutions. Waste cooking oil was collected from the local vendors.

2.2 Pretreatment of husk and catalyst preparation

The Ragi husk (RH) was completely washed with distilled water to eliminate the impurities and then dried in a hot air oven at 80 °C for 6 hours. The pretreatment of the RH was done via the acid leaching of the husk to get rid of the metal and mineral impurities present in it, especially the deleterious alkali, such as Na_2O and K_2O. 100 g of RH was added to a beaker containing 3N HCl and stirred for 3 hours at 80 °C, as shown in (Fig. 1). The husk was washed repeatedly with deionized water and dried at 80 °C for 4 hours. The dried husk was incinerated in a muffle furnace at 700°C for 4 hours, as shown in (Fig. 2), ensuring homogeneous distribution of the husk in the crucible as well as to ensure proper air circulation inside the muffle furnace, to produce Ragi husk ash (RHA). The study also further details that 700 °C is the critical temperature as burning below 700 °C results in the formation of residual carbon, and burning at temperatures, greater than 700 °C results in the formation of crystalline silica. The amorphous silica

Figure 1. Pre-treatment of Ragi husk.

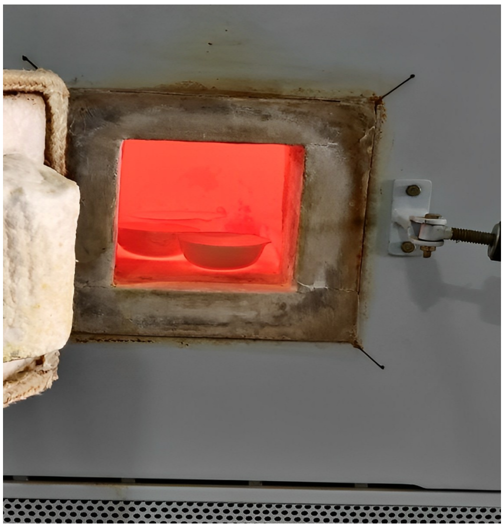

Figure 2. Incineration of Ragi husk.

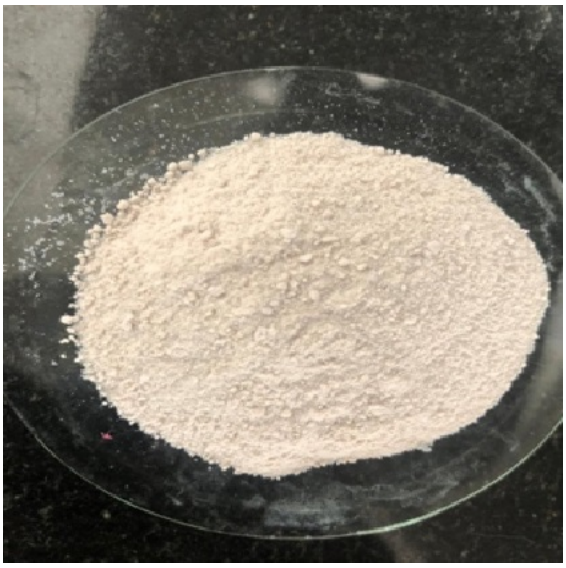

Figure 3. Sample of Ragi husk silica.

obtained from Ragi husk, as shown in (Fig. 3) with the above methodology, was crushed into powder and termed as RHSi. 6 g of RHSi was taken in a beaker, and 500 mL of 0.2M KOH was added to it. The suspension was obtained with continuous stirring, which was subjected to 80 °C for 3 h for the evaporation of water, and resulting in a concentrated slurry. The slurry was dried at 90 °C for 10 h followed by calcination at 650 °C for 3h and termed as K-RHSi.

2.3 Experimental procedure for synthesis of biodiesel

The transesterification reaction was performed with reactants such as waste cooking oil and methanol using K-RHSi as a heterogeneous catalyst. The oil was transferred into a 3-necked flask, and it was preheated at 65 °C for one hour. 3 w/w% of K-RHSi catalyst and methanol were introduced into the pretreated oil through continuous stirring. To the reaction mixture, 5 mL of methanol was added after 15 min, and the reaction was left to progress for 8 hours. The resulting mixture was added into a separating funnel, and the mixture was left for overnight.

The mixture resulted in two layers, the top being the biodiesel along with methanol and unreacted oil whereas the other layer is glycerol. For two hours, the top layer was placed in a hot air oven set at 120 °C to remove unreacted oil and methanol. After reducing to room temperature, the top layer was washed with hot water to separate unreacted oil, and the percentage yield of the biodiesel was measured.

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2.4 Characterization equipment

For X-ray diffraction (XRD), the instrument used is D8 ADVANCE, which was made by Bruker, Germany. It uses a 2.2 KW X-ray source with Cu anode, fine focus ceramic X-ray tube, and detector SSD 160-2 with 500 μm sensor. Thermogravimetry (DTA-TGA), the instrument used in TGA, is NETZSCH STA 449F5, made in Germany by the NETZSCH Group. Fourier Transform Infra-Red (FTIR), Scanning Electron Microscope (SEM), and Energy-dispersive X-ray spectroscopy analysis (EDS/EDX), the Hysitron PI 89 SEM is the instrument that was used to conduct the analysis. The samples were examined using Fourier Transform Infrared Spectroscopy (FTIR) to determine the type of chemical bonds present (PerkinElmer, Spectrum Two FT-IR IRL 1600300).

3. Results and discussion

3.1 Characterization of RHA

3.1.1 X-ray diffraction (XRD)

The XRD plot obtained for the Ragi husk silica, as shown in (Fig. 4), consists of a wide and broad peak between 15 °- 40 ° and peaks at 21.9 ° suggest the presence of silica. Similar results were reported in the literature by Sathi [16].

3.1.2 Thermogravimetry (DTA-TGA)

The DTA and TGA were performed to study the thermal stability of silica obtained from Ragi husk up to 700 °C as presented in (Fig. 5). The DTA curve shows two distinct stages of weight loss at about 10-120 °C as the first stage and 120-700 °C as the second stage. The loss in weight in the first stage, which can be seen with a decline in the DTG curve, is due to the desorption of absorbed water molecules,

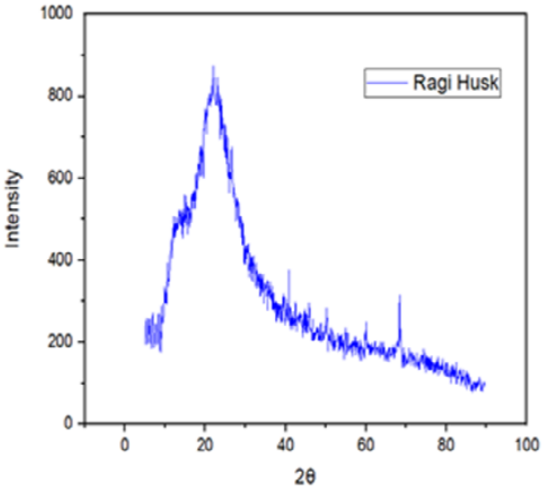

Figure 4. XRD pattern for Ragihusk ash.

and in the weight loss in the second stage is due to the loss of water by silanol groups condensation[17]. The burning of organic material, namely hemicelluloses and most of the starch, starts at approximately 10 °C and extends up to 150 °C. From 150 °C till to 700 °C, lignin undergoes decomposition. In the first stage, all the organic waste is decomposed.

3.1.3 Fourier transform infra-red (FTIR)

FTIR analysis was carried out to comprehend the structure and functional groups of the silica extracted from the Ragi husk (Fig. 6). The characteristic bands are located at 783.47-797.66 cm^{-1}, 1066.23-1071.09 cm^{-1}, 1659.10-1697 cm^{-1}, and 3205.03-3446.99 cm^{-1}, according to Figure 6. Puja P.N. and Similar outcomes were reported by [18], who recovered silica from rice and maize husks, respectively. The siloxane group (Si-O-Si) is shown by the bands between 616-797 cm^{-1} and 1037-1106 cm^{-1}, while the silanol group (Si-O-H) is shown by the bands between 1636-1641 cm^{-1} and 3204-3276 cm^{-1} bands between 1066.23 and 1071.09 cm^{-1} reflect the asymmetric stretching vibrations of the siloxane group (also known as ”Si-O-Si”), while those between 789 and 798 cm^{-1} represent the symmetric stretching vibrations.

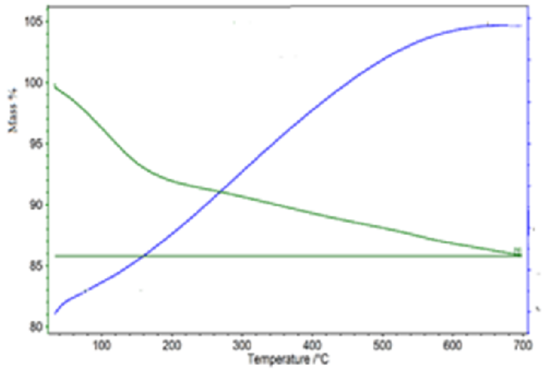

Figure 5. DTA-TGA curve for Ragihusk ash.

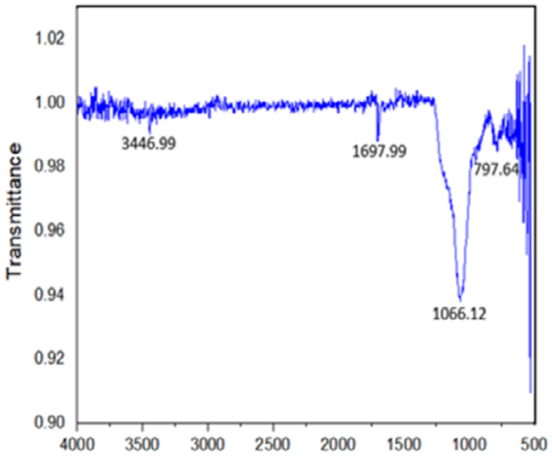

Figure 6. FTIR spectra for Ragi husk ash.

Bands at the wavelengths of 1631.51 to 1698.62 cm^{-1}, which correspond to the H-O-H bending vibrations, and 3204.39 to 3472.72 cm^{-1}, which correspond to the O-H bond stretching vibrations, were identified in the silanol group (Si-O-H). Similar bands at the same range were found by [19] and [20].

3.1.4 Scanning electron microscope (SEM)

The morphology of the Ragi husk silica was studied by making use of Scanning Electron Microscope (SEM) images. The SEM images obtained for the Ragi husk silica was shown in (Fig. 7), show an irregular particle size owing to rough, non-uniform grinding of the sample, and a flaky irregular particle shape.

3.1.5 Energy-dispersive X-ray spectroscopy analysis (EDS/EDX)

Energy-dispersive X-ray spectroscopy analysis (EDS/EDX), was used to determine the elemental composition of the amorphous silica samples. (Table 1) shows that the Ragi sample contains 52.83% and 40.72% by mass of oxygen and silicon, respectively, thereby showing a high purity of

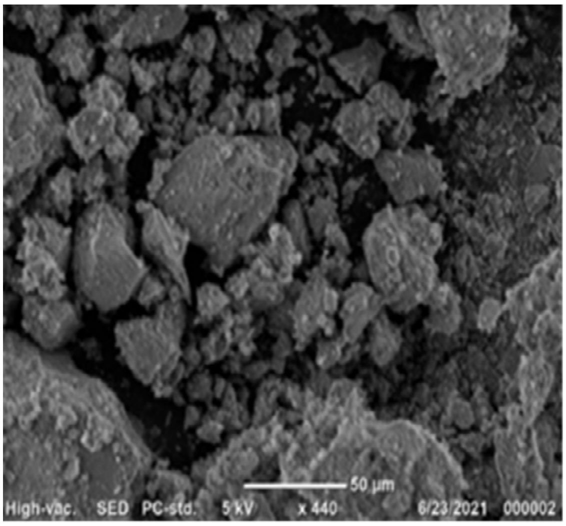

Figure 7. SEM image of Ragi husk ash.

SiO_2 in the sample. The Ragi sample has carbon as the most prominent trace impurity at 4.99% by mass.

3.2 Characterization results of catalyst(K-RHSi)

3.2.1 TGA analysis for K-RHSi

The weight loss in percentage of the potassium-incorporated Ragi husk ash catalyst is shown in (Fig. 8). The thermogram reveals that an initial weight loss below 200 °C is caused by the loss of water molecules that have been surface-adsorbed. In the temperature range between 200 °C and 700 °C, a small weight loss of 4% is observed, showing the produced catalyst's stability at higher temperatures.

Table 1. EDS results for Ragi husk ash.

Element	Weight%
O	52.83
Si	40.72
C	4.99
Zn	0.2
K,Fe	0.08,0.11
Cl	1.07

3.2.2 XRD pattern of K-RHSi

(Fig. 9) shows the powder XRD pattern of K-RHSi. The peaks at 27 and 29 degrees corresponds to K_2O phases con-

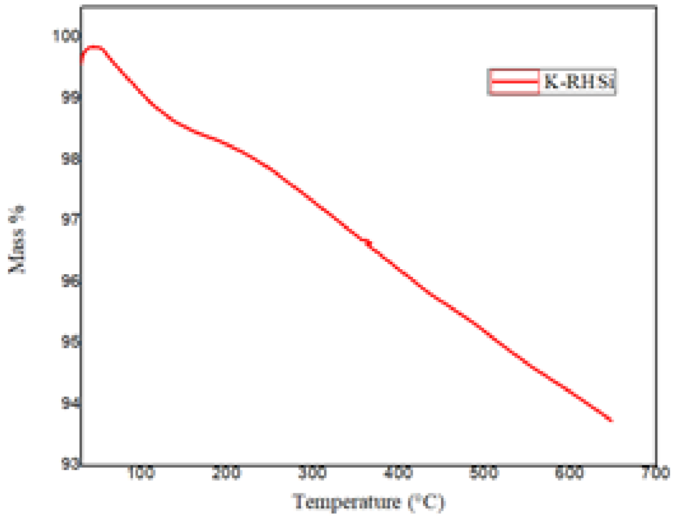

Figure 8. TGA of K-RHSi.

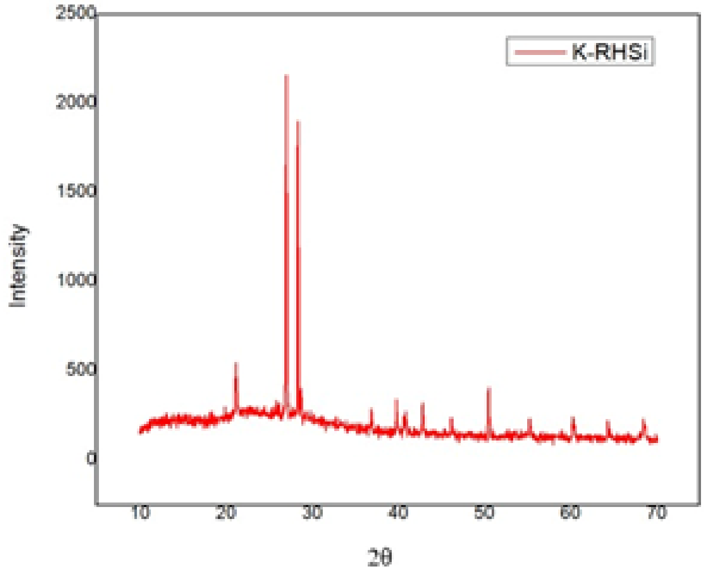

Figure 9. XRD pattern of K-RHSi.

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firmed by standard patterns. The minor peaks below 20 degrees are attributed to crystalline SiO_2 nature. From the XRD patterns, it was evident that the method of incorporation of potassium in SiO_2 followed by calcination at 650 °C resulted in proper dispersion of KOH into SiO_2.
The synthesized catalyst is suitable for biodiesel synthesis.

3.2.3 FTIR spectrum of K-RHSi

The K-RHSi FTIR spectra is shown in (Fig. 10). The peak in the 3500–3600 cm^{-1} range is caused by Si–OH vibrations. Because KOH was incorporated into SiO_2, the peak in K-RHSi was visible. O-Si-O symmetrical stretching vibrations are shown by the peaks at 1100 to 1200 cm^{-1}. The Si-O-Si vibrations are corresponding to the bands between 600 and 700 cm^{-1}.

3.2.4 Synthesized biodiesel

The biodiesel obtained at a 6:1 mole ratio (methanol: Oil), 3 w/w% at 65 °C resulted in an 83% yield of biodiesel. (Fig. 11) shows the FTIR spectrum of synthesized biodiesel and diesel. The frequency at 2800 to 3000 cm^{-1} and 1200 to 1300 cm^{-1} corresponds to the C-H stretching and CH_2 vibrations, respectively, of diesel and are in good correspondence to the methyl esters of biodiesel. These peaks, therefore, support that the triglycerides found in oil are transformed to methyl esters.

3.2.5 Properties of synthesized biodiesel

The biodiesel was tested for properties such as density (kg/m^3) 872.32, viscosity at 40 ° (mm^2/s) 4.123, flash point 145 °C, and pour point -4 °C. The obtained biodiesel prop-

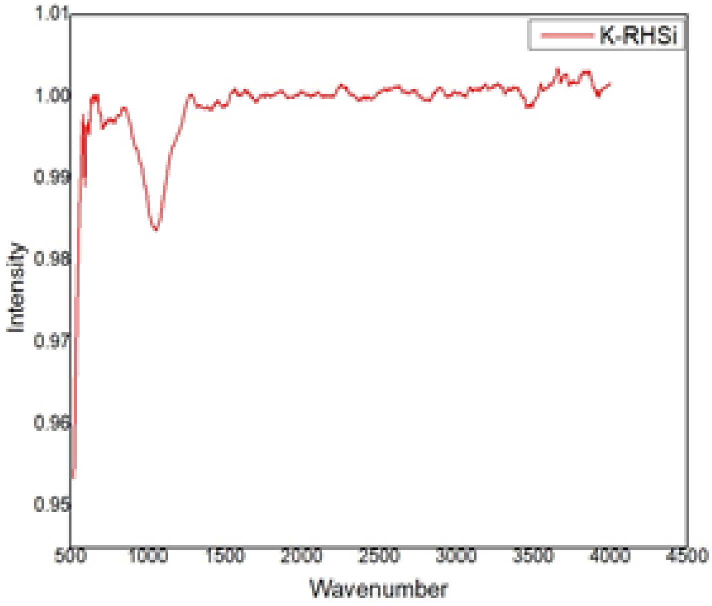

Figure 10. FTIR of K-RHSi.

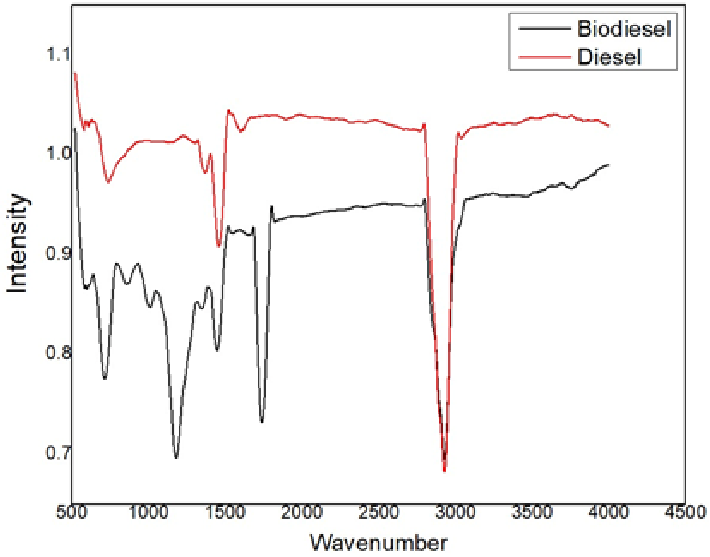

Figure 11. FTIR analysis of Diesel and Biodiesel.

erties are in good agreement with the ASTM standards.

3.2.6 Mechanism of transesterification reaction in biodiesel synthesis

The overall reaction in transesterification is shown in the Fig. 12. This reaction occurs in 3 major steps as given below.

Triglyceride + Methanol → Diglyceride + Alkyl ester
Diglyceride + Methanol → Monoglyceride + Alkyl ester
Monoglyceride + Methanol → Glycerol + Alkyl ester

The mechanism of alkaline-catalyzed methanolysis of triglyceride is shown in Fig. 13. Initially, an alkoxide is formed either from alkali metal alkoxides or from the reaction between an alkali and alcohol. This alkoxide then acts as a nucleophile, interacting with the carbonyl group of triglycerides to produce a primary tetrahedral intermediate. Subsequently, an alcohol reacts with this intermediate, regenerating the alkoxide and forming a secondary tetrahedral intermediate, which eventually yields an alkyl ester and diglyceride. The regenerated active alkoxide can then initiate another catalytic cycle by attacking another carbonyl group of the glycerides. Ultimately, through similar catalytic cycles, diglycerides and monoglycerides are converted into glycerols and a mixture of alkyl esters, representing the final products. M represents Metal alkoxide and R represents alkyl group.

3.3 Reusability of catalyst

The K-RHSi catalyst was separated from the reaction mixture by filtration and further washed with solvent n-hexane to remove any dissolved impurities. The catalyst was dried in the oven at 80 °C for 8 hours. The catalyst is further used in the transesterification reaction. Fig. 14 represents the reusability studies. It can be observed that the yield of

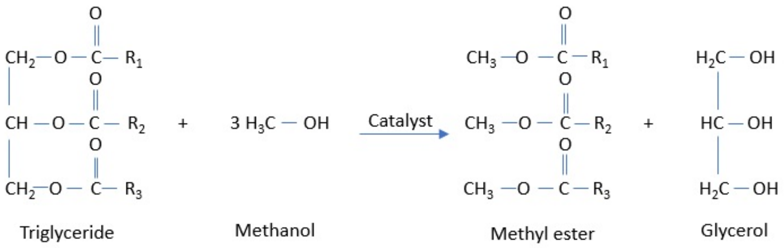

Figure 12. Transesterification reaction.

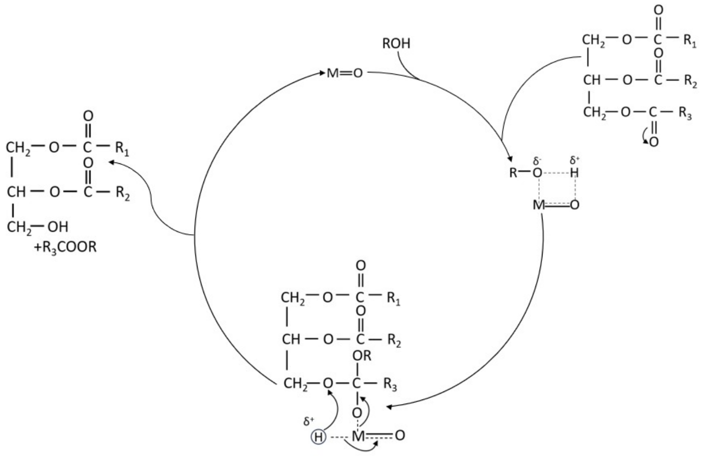

Figure 13. Mechanism of transesterification reaction in presence of alkaline catalyst.

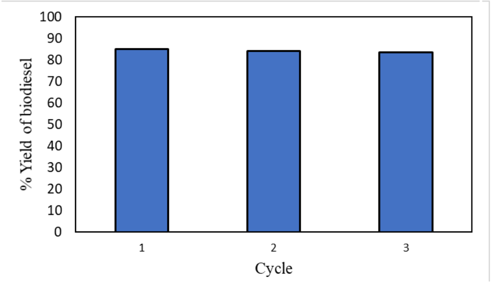

Figure 14. Reusability studies.

Table 2. Synthesis of biodiesel using various catalysts.

S.No	Reactants	Catalyst	Reaction parameters	Yield of biodiesel	Ref
1	Waste cooking oil and methanol	KOH impregnated on naturally available SiO_2	8:1 mole ratio (methanol: Oil), 2-5 w/w % at 60°C	85%	[21]
2	Sunflower oil and methanol	NaOH impregnated on naturally available SiO_2	6:1 mole ratio (methanol: Oil), 3 w/w % at 60°C	94%	[22]
3	Sunflower vegetable oil and methanol	KOH impregnated on Fumed silica	12:1 mole ratio (methanol: Oil), 3 w/w % at 60°C	99%	[23]
4	Waste vegetable oil and methanol	KOH impregnated on diatomite	Methanol to oil 30% by mass, 5 w/w% at 60°C	90%	[24]
5	Waste Cooking oil and methanol	CaO impregnated on SiO_2	15:1 mole ratio (methanol: Oil), 6 w/w % at 60°C	94%	[25]
6	Waste cooking oil and methanol	K-RHSi	6:1 mole ratio (methanol: Oil), 3 w/w % at 65°C	83%	Present Work

biodiesel has decreased from 85% to 83% in the 3rd cycle, indicating the catalyst exhibits low deactivation.

3.4 Comparison with the literature

Table 2 presents the comparison of various catalysts employed for biodiesel synthesis. The present catalyst exhibited a yield of 85% using waste cooking oil at mole ratio of 6:1, catalyst loading 3 w/w % at 65 °C. Since ragi husk is widely available and the silica is easy to extract, the current technology for producing biodiesel is both affordable and environmentally friendly. The 85% yield obtained in this work may have been caused by contaminants found in the used cooking oil.

4. Conclusion

The extraction of silica from Ragi husk was carried out, and the obtained amorphous silica samples were characterized using XRD, FTIR, SEM as well as EDS analysis, and it was evident from XRD and FTIR that the Ragi crop residues contained a significant amount of SiO_2 that was easily extractible, with the optimal incineration parameters being 700 °C and 4 hours. The SEM and EDS results also indicate that the product obtained is amorphous and of high purity, the Ragi husk silica containing 52.83% and 40.72% by mass of oxygen and silicon. The KOH impregnated on Ragi husk has proved to be a potential catalyst support for the synthesis of biodiesel resulting in 83% yield. The obtained biodiesel exhibited good fuel properties as compared to commercial diesel. The present work shows a sustainable and economical path to a biofuel industry.

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Authors Contributions
Authors have equal contribution role in preparing the paper.

Availability of Data and Materials
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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

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