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Biodiesel Production from Waste Plant Oil over a Novel Nano-Catalyst of Li-TiO_2/Feldspar

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Abstract: A novel Li-impregnated TiO_2 catalyst loaded on feldspar mineral (Li-TiO_2/feldspar) was synthesized via a wet impregnation method and was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) analysis. Using these techniques, it was possible to confirm the catalyst's structural organization with a high crystallinity. This catalyst was used in the transesterification of five waste plant oils of *Citrullus colocynthis* (bitter apple), *Pongamia pinnata* (karanja), Sinapis arvensis (wild mustard), *Ricinus communis* (castor) and *Carthamus oxyacantha* (wild safflower). The catalytic tests were performed at temperatures ranging from 40 to 80 °C, employing a variable methanol/ester molar ratio (5:1, 10:1, 15:1, 20:1 and 25:1) and different catalyst concentrations (0.5%, 1%, 1.5%, 2% and 2.5%) relative to the total reactants mass. Conversion of 98.4% of fatty acid methyl esters (FAMEs) was achieved for *Pongamia pinnata* (karanja). The main fatty acids present in bitter apple, karanja, wild mustard, castor and wild safflower oils were linoleic acid (70.71%), oleic acid (51.92%), erucic acid (41.43%), ricinoleic acid (80.54%) and linoleic acid (75.17%), respectively. Li-TiO_2/feldspar produced more than 96% for all the feedstocks. Fuel properties such as iodine value (AV), cetane number (CN), cloud point (CP), iodine value (IV), pour point (PP) and density were within the ranges specified in ASTM D6751.

Keywords: Li-TiO_2; catalyst; feldspar; biodiesel; wild mustard

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1. Introduction

The world's primary sources of energy are fossil fuels, but due to the limited reservoirs remaining and the production of huge amounts of greenhouse gases during combustion, they are non-viable energy sources [1]. The emissions resulting from fossil fuel combustion adversely affect both the environment and human health [2]. Fossil fuels are continuous sources of emissions. Biodiesel (BD) is a useful alternative to fossil fuels [3]. BD comprises mono-alkyl esters of long-chain fatty acids (FA) [4]. Biodiesel is a renewable and biodegradable clean-burning fuel with low exhaust emissions.

The increasing interest in BD production is due to its ability to use unlimited feedstocks. High yield and low production cost are most significant aspects of ideal feedstocks. Usually, the raw material cost covers ~60–80% of the total production cost of BD [5]. The best feedstocks for biodiesel production have a low cost, high oil contents and are regionally available [6]. Different edible oils and microorganisms such as bacteria, microalgae, yeast, and fungi can be used for biodiesel production [7]. Edible plants as feedstocks for biodiesel are not good candidates for biodiesel production, as this will result in increased food prices [8]. The manufacturing cost has increased 70–92% because of the rise in edible oils' cost, thus stimulating biodiesel manufacturing from non-edible oils [9]. The use of non-edible oils removes the food verses fuel debate related to biodiesel's production from edible oils [10]. Moreover, non-edible oils are more efficient, economical, and environmentally friendly, and the reduce the deforestation rate, as they are easily available in wastelands

that are not appropriate for food crops. Recently, non-edible oils have been considered as potential feedstocks for BD production. *Pongamia pinnata*, usually known as karanja, is a medium-sized glabrous perennial tree that grows in littoral regions of Australia and Southeastern Asia. The yield is 8–24 kg of oilseed per tree [11]. *Carthamus oxyacantha* is a 1.5 m-tall, spiny-leaved annual herb, belonging to the family Asteraceae, generally known as wild safflower. This species is not eaten by livestock. It also reduces the yield of cereal crops [12]. It grows on any land and has no production costs prior to harvesting operation. It is resistant to harsh environmental conditions and dry climates [13]. *Citrullus colocynthis* plant oil was discovered as a new option for biodiesel production. Its seeds contain 47% oil. *Sinapis arvensis* L. (wild mustard) is a wild plant with high oil yields. It grows in calcareous soils. *Ricinus communis* (castor plant) can also be explored as a potential resource for BD production. Its seeds contain 40–60% oil.

All vegetable oils are very viscous, and their viscosities are 10–20 times higher than that of diesel fuel [14]. To overcome the challenges associated with vegetable oils, an effective method is the conversion of these oils into FAME [11]. The most common and widely accepted method for biodiesel production is transesterification. Transesterification is a reaction between triglyceride from vegetable oils/animal fats and alcohol using a catalyst [15]. Transesterification requires normal conditions and provides the best quality and efficiency of converted fuel [16]. Biodiesel and glycerol are produced during transesterification [17]. Glycerol, a valuable byproduct of this reaction, is used in various industries [18].

The overall cost of the process will increase and requires a long time for transesterification in the absence of a catalyst [1]. Homogenous and heterogeneous catalysis are conventionally carried out to produce biodiesel. Heterogeneous catalysts are better than homogeneous catalysts because they are easier to use, experience less contamination of the product and co-products, their separation from the medium is easier, and they option of regeneration and reuse [19]. Some drawbacks of these catalysts include the requirement for a greater quantity and availability of surface area, which results in reduced overall catalytical activity. Hence, heterogenous nano-catalysts could play a prominent role not only in producing higher yields of biodiesel, but also a better quality in a shorter reaction time. TiO_2 has gained popularity as a heterogenous catalyst because of its mesoporous structure, providing it with a larger surface area and several additional properties such as environmental friendliness, durability and low cost as compared to conventional nanomaterials [20]. Lithium doping of TiO_2 increases its transesterification ability significantly [19].

The catalytic supports could play an effective role in the production and separation of catalysts from the reaction mixtures. The primary role of the catalytic support is to provide stability to small metal catalyst particles [21]. The catalyst supports not only provide support to catalysts, but are also helpful in increasing their surface area [22]. The most used catalytic supports are zirconium dioxide, aluminum oxides, alumino silicates, magnesium oxide, silica gel, and titanium oxide. The use of clay materials has some advantages as compared to other supports, such as operational simplicity, high selectivity, low cost, and reusability [23]. Feldspar comprises more than half of the Earth's crust and is the most abundant mineral. Feldspar minerals consist of tectosilicates. Tectosilicates are silicate minerals containing silicon ions linked by shared oxygen ions to form a 3D network. Hence, feldspar provides a 3D surface area for catalyst anchoring [24]. The current study is focused on biodiesel synthesis using a novel Li-impregnated TiO_2 catalyst loaded on feldspar minerals.

The current study is focused on biodiesel production from waste plant oils of *Citrullus colocynthis*, *Pongamia pinnata*, *Sinapis arvensis*, *Ricinus communis*, and *Carthamus oxyacantha*, utilizing a Li-incorporated titanium oxide catalyst supported on feldspar minerals (Li-TiO_2/feldspar). The catalytical support was also prepared from waste or low-cost materials including clay minerals. Lithium-doped TiO_2 supported on feldspar has been used as a low-cost novel catalyst for the conversion of waste seed oils into biodiesel.

2. Results and Discussion

2.1. Seed Oil Yield (%)

Oil was extracted from ground seeds of five different nonedible feedstocks such as *Pongamia pinnta* (karanja), *Sinapis arvensis* (wild mustard), *Carthamus oxyacantha* (wild safflower), *Ricinus communis* (castor oil) and *Citrullus colocynthis* (bitter apple) by means of the screw press method. The percentage oil yield of the five different plants using 20 kg of seeds of each feedstock is shown in Table 1. The oil content of the extracted castor oil, karanja, wild mustard, wild safflower, and bitter apple seeds before the conversion to biodiesel (crude oil) was 39.2%, 37.05%, 32.5%, 29.55%, and 17.95%, respectively. The percentage oil yield was calculated using Equation (1).

$$Yield\ \% = \frac{Weight\ of\ oil}{Weight\ of\ seeds} \times 100 \quad (1)$$

Table 1. Percentage oil yield of five different seeds.

Seeds Type	Seed Weight (kg)	Oil Weight (kg)	Yield (%)
Karanja	20	7.41	37.05
Wild mustard	20	6.50	32.5
Wild safflower	20	5.91	29.55
Castor oil	20	7.84	39.2
Bitter apple	20	3.59	17.95

2.2. X-ray Diffraction (XRD) Analysis

Feldspar has a main sample peak of $KAlSi_3O_8$ in XRD spectra, as shown in Figure 1a. Intense sharp diffraction peaks were observed in XRD at a low angle position, 2θ = 26.63°, which shows mesopores with a uniform diameter. The diffraction peaks at 2θ of 20.86°, 36.54°, 39.49°, 40.28°, 42.44°, 45.78°, 50.14°, 54.87°, 55.318°, 59.95°, 60.12°, 64.06°, 67.73°, 68.12°, 68.3° were identified, showing the single phase of a highly ordered structure. The crystal size was calculated from the Debye–Scherrer equation. The average size of feldspar crystals was 41.83 nm.

Since the catalyst with 20% Li content provided the highest conversion yield, the XRD pattern of 20% Li-TiO_2 supported on feldspar is shown in Figure 1b. The diffraction peaks were assigned to the Li_2TiO_3 phase at 2θ of 20.65°, 36.38°, 39.2°, 54.68° and 59.80°. Li_2O diffraction peaks were not detected for Li-loaded samples, as also noted previously [25]. Feldspar showed intense sharp diffraction peaks at 2θ = 26.65°, 50°, 67.96°. The average crystallite size of the Li-TiO_2/feldspar catalyst was determined as 19 nm by means of the Scherrer equation, and thus the catalyst exhibited a nanoparticle character. The higher particle size has a lower surface area.

2.3. Fourier Transform Infrared Specroscop (FTIR) Analysis

The FTIR spectrum of feldspar is shown in Figure 2a. Feldspars are igneous aluminosilicate minerals. The absorption peaks shown by pure feldspar at 775.3, ~776, 693, 1080 cm^{-1} were due to the stretching vibration of Si–O–Si, the SiO_2 bearing bond, the bending vibrations of silicon-oxygen, and the stretching vibrations of Si–O–Al, respectively. H–O–H bending vibrations were observed at 2102 cm^{-1} and 2318 cm^{-1} [26,27].

The FTIR spectrum of 20% Li-TiO_2 supported on feldspar is shown in Figure 2b. The bands at 1507 cm^{-1} and 1457 cm^{-1} are assigned to the specific characteristic of the Li–O–Ti bond [28]. The small band at the wavelength of 1090 cm^{-1} can be ascribed to the presence of aluminosilicates. The peaks at 2322 cm^{-1}, 2342 cm^{-1} and 2372 cm^{-1} were due to H–O–H bending vibration.

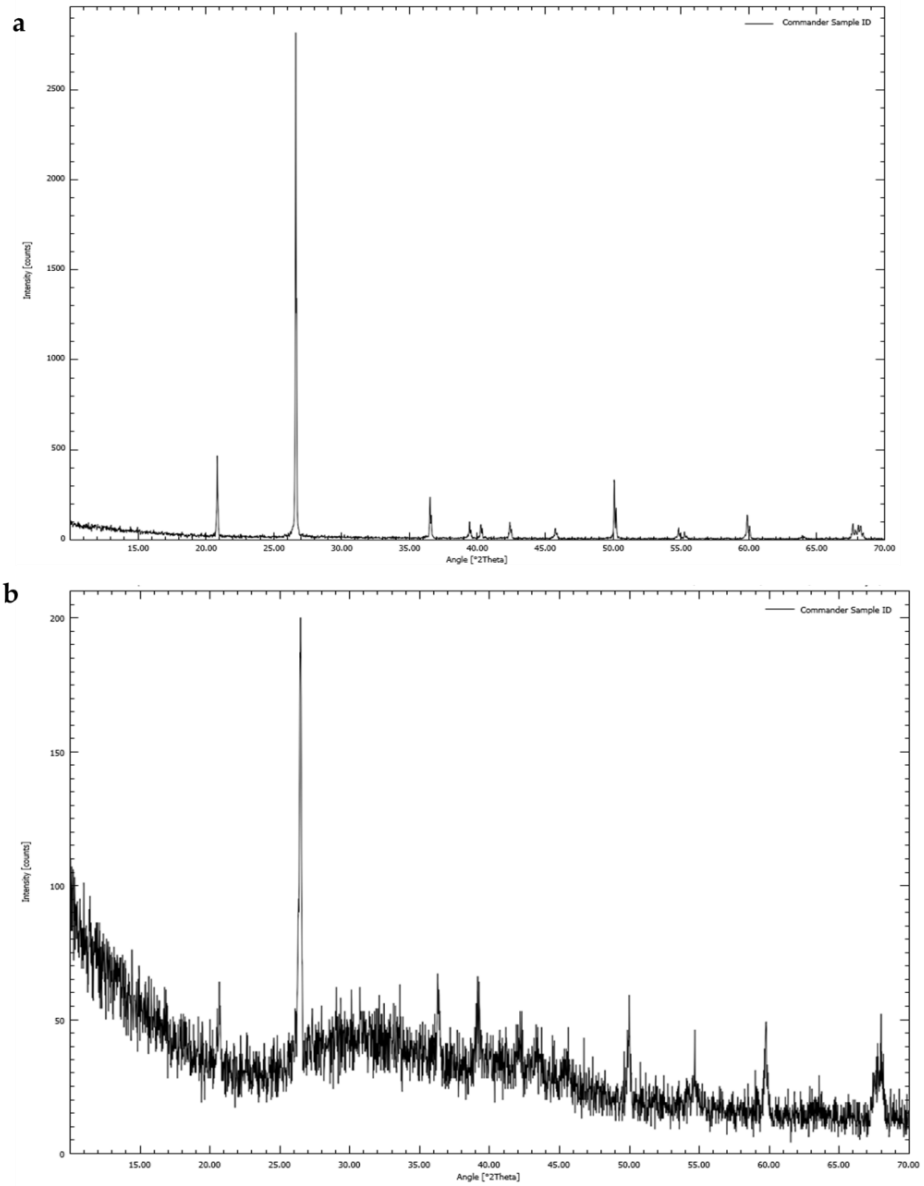


Figure 1. XRD of (**a**) feldspar (catalyst support) and (**b**) 20% Li-TiO_2/feldspar.

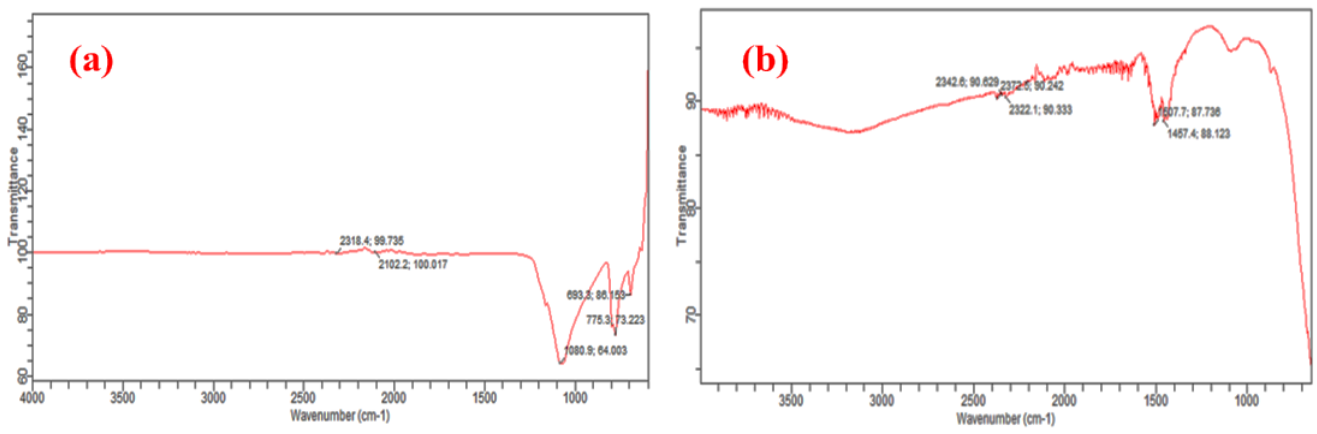
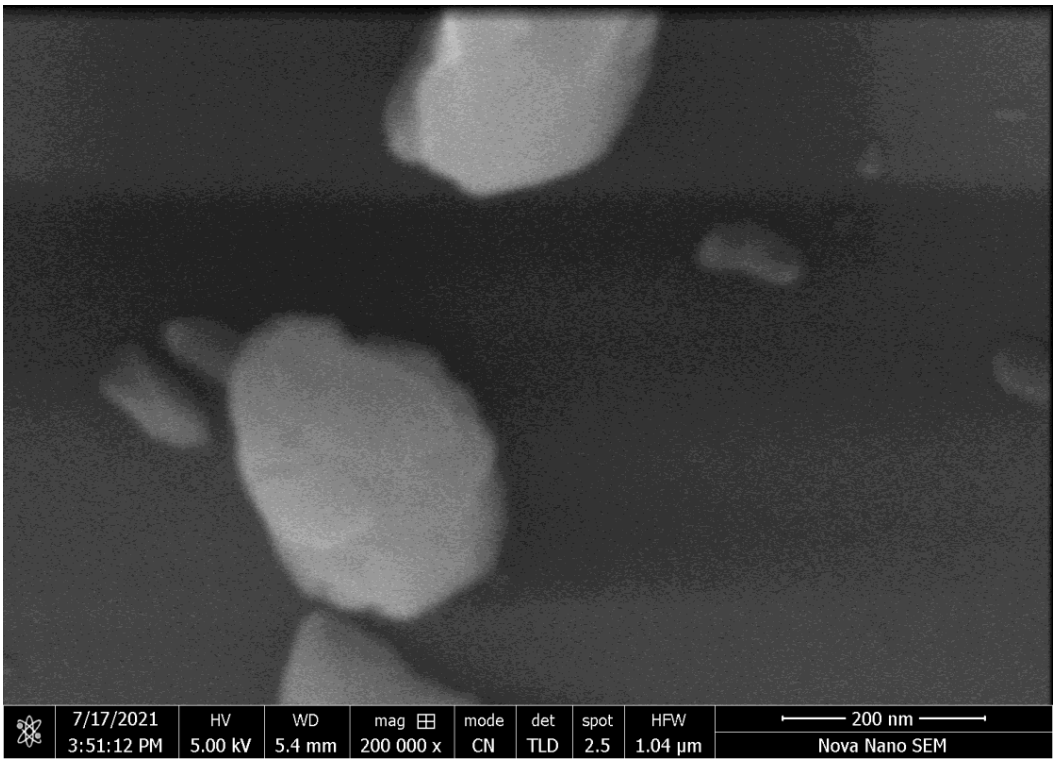


Figure 2. FTIR of (**a**) feldspar and (**b**) 20% Li-TiO_2/feldspar.

2.4. Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Analysis (EDX) Analysis

SEM/EDX for feldspar nanoparticles can be seen in Figure 3. The obtained micrographs of samples were of high crystallinity and non-uniform size. The K-feldspar showed a mesoporous lamellar structure. Due to its multiplicity and complex interfaces, a crossed-lamellar structure provides a high surface area [29,30].

(a)



(b)

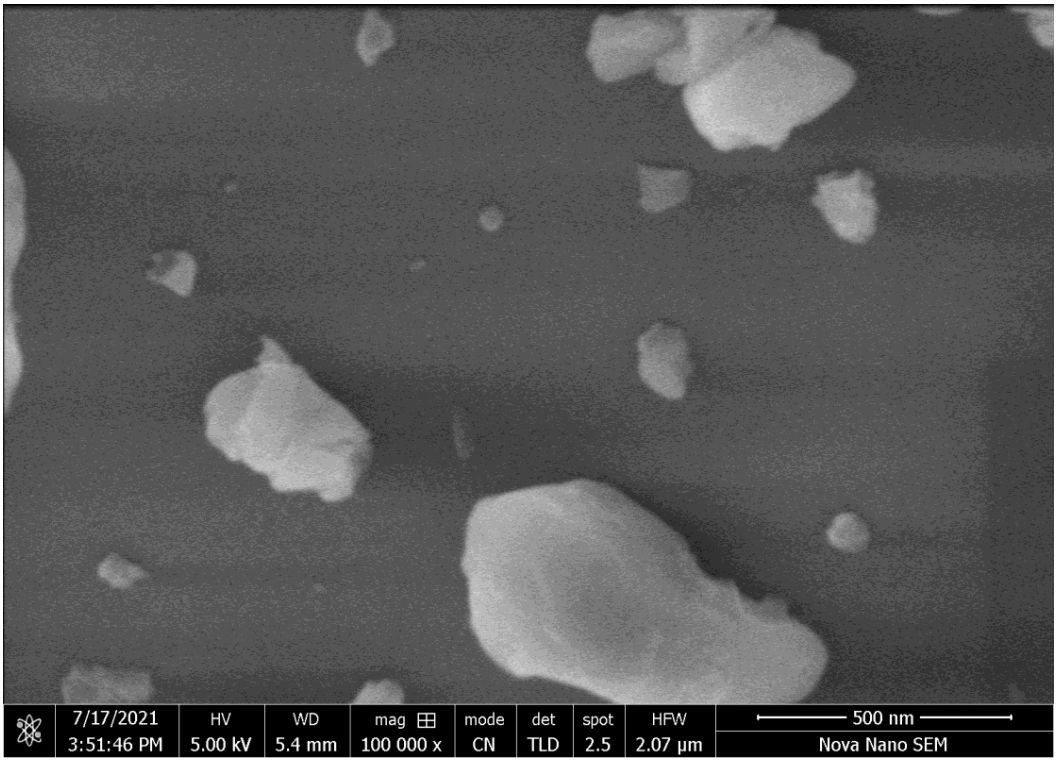


Figure 3. *Cont.*

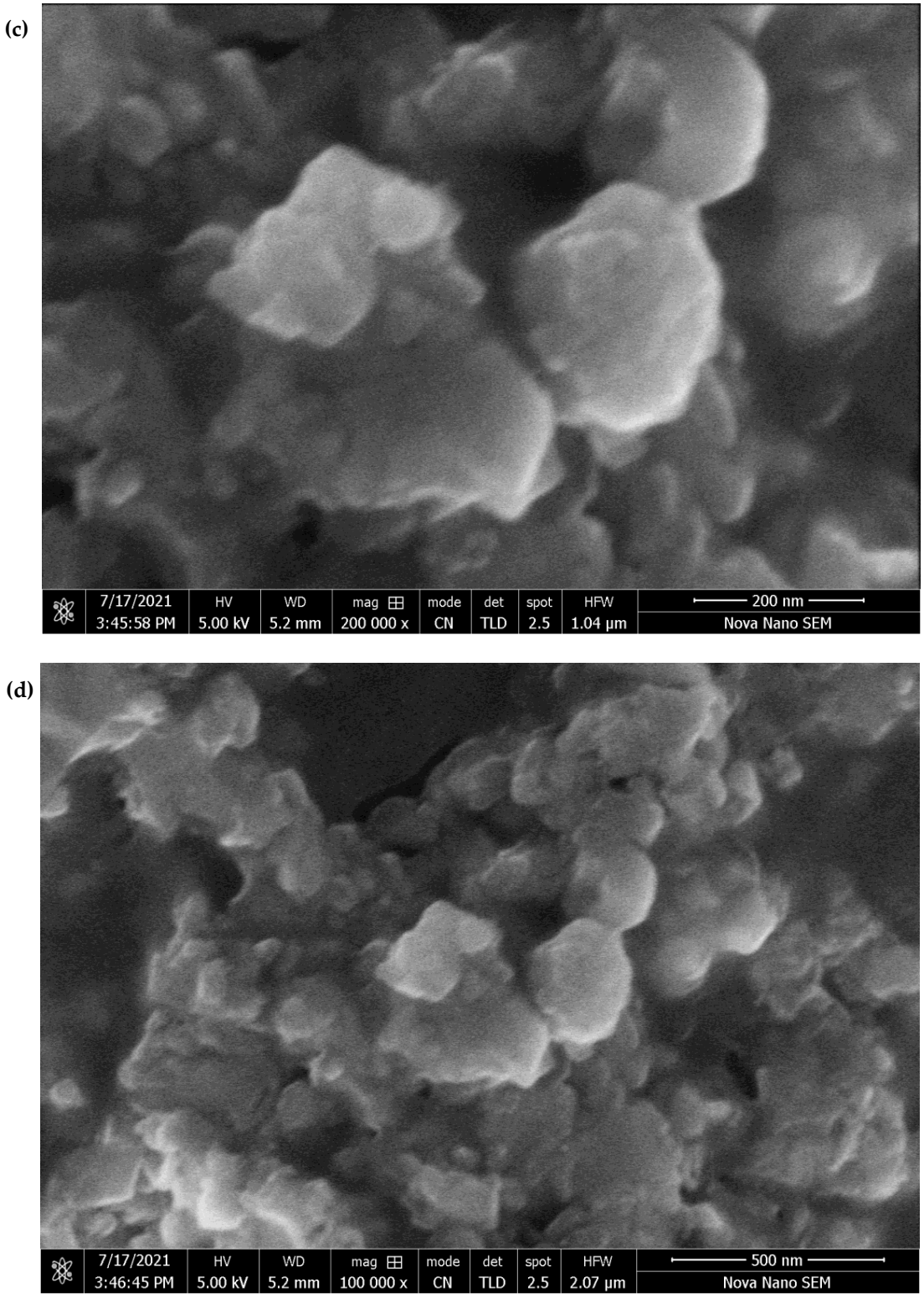


Figure 3. SEM images of (**a**) feldspar at 200 nm, (**b**) feldspar at 500 nm, (**c**) Li-TiO_2/feldspar at 200 nm, (**d**) Li-TiO_2/feldspar at 500 nm.

The SEM/EDX images of Li-TiO_2 supported on feldspar are displayed in Figure 3. SEM image shows the presence of embedded grains without sharp boundaries. The agglomeration of small grains to form large grains can be clearly observed in the images. This resulted in the appearance of small nano holes on the surface of the composite [31]. The dark spots represent the porosity in the sample. Porous materials increase the specific sur-

face area and thus increase the catalytic activity. The EDX spectrum for Li-TiO_2 supported on feldspar was obtained in order to confirm the chemical composition of the sample. The spectrum depicts (Figure 4) the presence of all of the elements, i.e., O, Si, Ti, Fe and Al, with weight percentages of 57.75%, 18.77%, 5.68%, 1.22% and 0.75%, respectively. All of the elements in the sample were detected, except for lithium (Li), due to the inability of the EDX technique to detect small-Z elements [32].

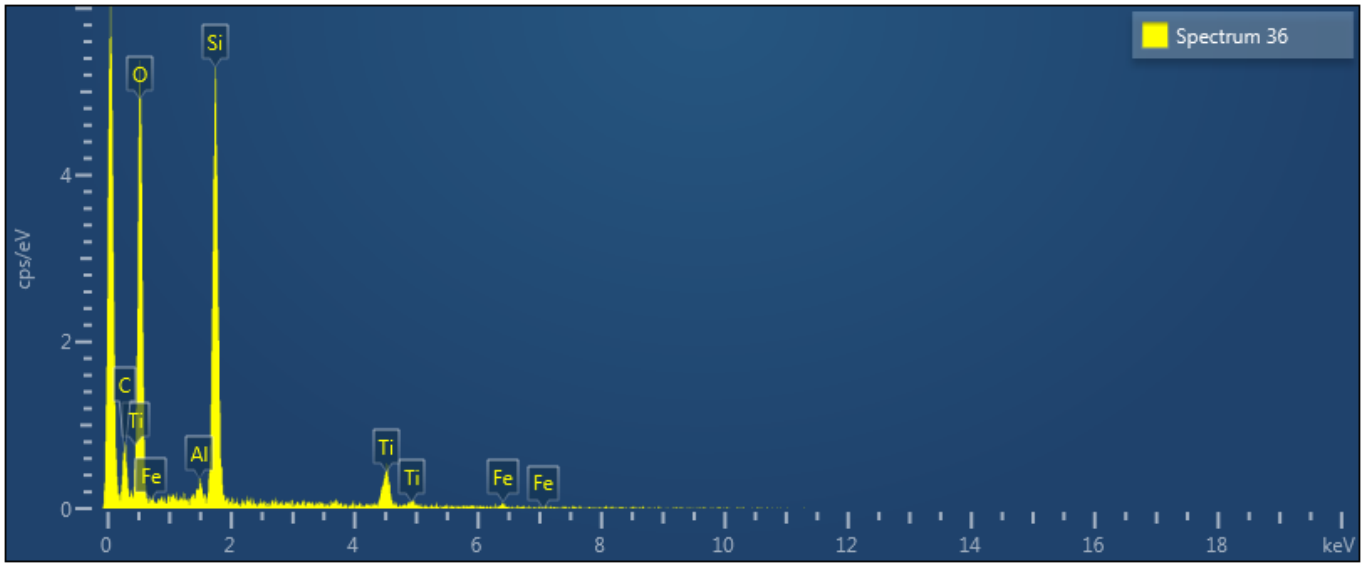


Figure 4. EDX of 20% Li-TiO_2/feldspar.

2.5. Effect of the Li to TiO_2 Percentage Weight Ratio

The weight ratio of the Li to TiO_2 percentage is shown in Table 2. The results show that impregnation with 20 wt% Li exhibited the highest conversion under the reaction conditions of a 5:1 methanol:oil ratio, for a reaction time of 120 min, at 40 °C and with a 1% catalyst concentration.

Table 2. Biodiesel yield (%) using Li-TiO_2/feldspar nanocatalysts.

Catalyst	Biodiesel Yield (%)				
	Karanja	**Wild Mustard**	**Castor**	**Wild Safflower**	**Bitter Apple**
10% Li/TiO_2/feldspar	85.0 ± 0.5	81.0 ± 0.8	76.6 ± 0.2	83.0 ± 0.9	78.2 ± 0.2
20% Li/TiO_2/feldspar	86.1 ± 0.8	89.1 ± 0.5	87.4 ± 0.3	89.7 ± 0.3	88.3 ± 0.9
30% Li/TiO_2/feldspar	84.4 ± 0.8	83.5 ± 0.8	80.0 ± 0.8	79.1 ± 0.3	80.3 ± 0.7
40% Li/TiO_2/feldspar	85.4 ± 0.4	80.2 ± 0.4	84.1 ± 0.6	83.0 ± 0.3	82.4 ± 0.5

2.6. Optimization of Process Parameters

Bitter apple, karanja, wild mustard, castor, and wild safflower oil transesterification was tested under different reaction conditions to obtain the maximum yield. Since the 20 wt% loading amount of lithium provided the highest production value, all investigations were further conducted with 20% Li-TiO_2/feldspar catalyst.

2.6.1. Effect of Catalyst Concentration

The biodiesel yield depends upon the catalyst concentration. The effect of selected supported nanocatalysts on methyl ester yield from bitter apple, karanja, wild mustard, castor, and wild safflower oils is depicted in Tables 3–7. The influence of catalyst amount

was examined by changing the catalyst amount within a range of 0.5–2.5% (wt. of catalyst/wt. of oil). The other operational conditions were kept constant (temperature (40 °C), time (120 min) and methanol to oil ratio (5:1)) using five different feedstocks.

Table 3. Yield of biodiesel from karanja oil with changes in reaction parameters.

Feedstock	Conc. of Catalyst (%)	Methanol to Oil Ratio	Temperature (°C)	Reaction Time (min)	Biodiesel Yield (%)
Karanja	0.5	5:1	40	120	84.5 ± 0.8
	1.00				86.1 ± 0.7
	1.5				86.0 ± 0.6
	2.00				89.3 ± 0.5
	2.5				87.0 ± 0.4
	2.00	10:1	40	120	91.7 ± 0.6
		15:1			88.0 ± 0.4
		20:1			86.5 ± 0.9
		25:1			83.7 ± 0.7
	2.00	10:1	50	120	98.4 ± 0.9
			60		93.4 ± 0.5
			70		90.0 ± 0.6
			80		87.0 ± 0.8
	2.00	10:1	50	30	87.1 ± 0.1
				60	89.3 ± 0.6
				90	90.0 ± 0.7
				150	93.1 ± 0.7

Table 4. Yield of biodiesel from wild mustard oil with changes in reaction parameters.

Feedstock	Conc. of Catalyst (%)	Methanol to Oil Ratio	Temperature (°C)	Reaction Time (min)	Biodiesel Yield (%)
Wild mustard	0.5	5:1	40	120	86.0 ± 0.5
	1.00				89.1 ± 0.3
	1.5				87.1 ± 0.9
	2.00				85.0 ± 0.5
	2.5				84.2 ± 0.7
	1.00	10:1	40	120	87.1 ± 0.8
		15:1			85.3 ± 0.4
		20:1			83.6 ± 0.5
		25:1			81.5 ± 0.3
	1.00	5:1	50	120	94.7 ± 0.8
			60		89.0 ± 0.6
			70		84.0 ± 0.7
			80		80.0 ± 0.4
	1.00	5:1	50	30	88.2 ± 0.2
				60	91.2 ± 0.9
				90	96.7 ± 0.7
				150	90.5 ± 0.6

In the presence of 20% Li-TiO_2/feldspar, bitter apple, castor, wild mustard, and wild safflower oil provided the highest yield at 1%. The highest biodiesel yield from bitter apple, castor, wild mustard, and wild safflower was 88.3 ± 0.4%, 87.4 ± 0.4%, 89.1 ± 0.3% and 89.7 ± 0.3%, respectively.

Table 5. Yield of biodiesel from wild safflower oil with changes in reaction parameters.

Feedstock	Conc. of Catalyst (%)	Methanol to Oil Ratio	Temperature (°C)	Reaction Time (min)	Biodiesel Yield (%)
Wild safflower	0.5	5:1	40	120	86.1 ± 0.6
	1.00				89.7 ± 0.3
	1.5				87.2 ± 0.4
	2.00				85.3 ± 0.2
	2.5				85.0 ± 0.9
	1.00	10:1	40	120	88.0 ± 0.7
		15:1			86.3 ± 0.8
		20:1			84.5 ± 0.5
		25:1			82.7 ± 0.7
	1.00	5:1	50	120	96.5 ± 0.3
			60		92.5 ± 0.6
			70		90.0 ± 0.8
			80		89.5 ± 0.7
	1.00	5:1	50	30	91.4 ± 0.6
				60	94.2 ± 0.7
				90	96.5 ± 0.8
				150	95.0 ± 0.9

Table 6. Yield of biodiesel from bitter apple oil with changes in reaction parameters.

Feedstock	Conc. of Catalyst (%)	Methanol to Oil Ratio	Temperature (°C)	Reaction Time (min)	Biodiesel Yield (%)
Bitter apple	0.5	5:1	40	120	87.0 ± 0.5
	1.00				88.3 ± 0.4
	1.5				86.0 ± 0.7
	2.00				85.0 ± 0.6
	2.5				83.9 ± 0.4
	1.00	10:1	40	120	89.2 ± 0.7
		15:1			86.5 ± 0.6
		20:1			83.4 ± 0.9
		25:1			80.7 ± 0.8
	1.00	10:1	50	120	96.2 ± 0.8
			60		90.0 ± 0.3
			70		87.0 ± 0.5
			80		84.0 ± 0.6
	1.00	10:1	50	30	89.2 ± 0.6
				60	91.4 ± 0.7
				90	94.5 ± 0.8
				150	93.6 ± 0.2

However, karanja provided the highest biodiesel yield (89.3 ± 0.5%) at a catalyst concentration of 2%. The overall results of the effect of catalyst concentration on biodiesel yield are quite promising and indicate that a certain level of catalyst concentration is required to obtain the maximum biodiesel yield. The optimized concentration level was not only dependent upon the type of catalyst/support used, but was also dependent on the type of oil under investigation. Catalysts at low concentrations could not effectively drive reactions. At high catalyst concentrations, a viscous emulsion formed in the reaction mixture, which restricted the effective mass transfer of the reactants onto the active surface of catalyst, causing diffusion and saturation, thus hindering the interaction. The result is the overall reduced product yield [33].

Table 7. Yield of biodiesel from castor oil with changes in reaction parameters.

Feedstock	Conc. of Catalyst (%)	Methanol to Oil Ratio	Temperature (°C)	Reaction Time (min)	Biodiesel Yield (%)
Castor oil	0.5	5:1	40	120	86.1 ± 0.8
	1.00				87.4 ± 0.4
	1.5				85.0 ± 0.6
	2.00				84.1 ± 0.9
	2.5				83.4 ± 0.6
	1.00	10:1	40	120	88.3 ± 0.8
		15:1			90.0 ± 0.4
		20:1			87.7 ± 0.8
		25:1			85.0 ± 0.6
	1.00	15:1	50	120	91.0 ± 0.7
			60		96.1 ± 0.3
			70		89.0 ± 0.4
			80		87.0 ± 0.6
	1.00	15:1	60	30	90.5 ± 0.5
				60	93.1 ± 0.7
				90	96.1 ± 0.6
				150	94.5 ± 0.8

2.6.2. Effect of Methanol to Oil Ratio

The effect of methanol to oil ratio was studied at five different levels including 5:1, 10:1, 15:1, 20:1 and 25:1 (methanol:oil) for the 20% Li-TiO_2/feldspar catalyst to optimize biodiesel production from bitter apple, karanja, wild mustard, castor and wild safflower oils. The methanol/oil molar ratio is one of the most vital factors affecting biodiesel yield. Although the theoretically required methanol/oil molar ratio is 3:1, it is commonplace to carry out the transesterification reaction with an extra amount of alcohol to shift the equilibrium to the fatty acid methyl ester (FAME) side. The optimum molar ratio of alcohol is very important to reduce the production cost of biodiesel. At a lower alcohol molar ratio, the conversion of triglycerides into FAME will not be complete. On the other hand, a very high molar ratio may also decrease biodiesel yield, as methanol can cause emulsification of the polar hydroxyl groups present in glycerol, which is a byproduct of biodiesel production. This emulsification process hinders forward reactions and favors backward reactions. As a result, a decrease in the biodiesel yield is observed. An optimized amount of alcohol (a slight excess amount) is required to keep the transesterification reaction in the forward direction, as the transesterification reaction is reversible in nature [34]. The effect of the methanol to oil ratio on biodiesel production is summarized in Tables 3–7.

The optimum methanol to oil ratio was 10:1 for karanja and bitter apple using 20% Li/TiO_2/feldspar. The highest biodiesel yield obtained from karanja and bitter apple was 91.7 ± 0.6 and 89.2 ± 0.7, respectively, while wild mustard and wild safflower provided the maximum biodiesel yield (89.1 ± 0.3 and 89.7 ± 0.3%, respectively) at a 5:1 methanol to oil ratio.

It can be noted from the obtained results that castor oil requires a 15:1 methanol to oil ratio, which is relatively higher than the other oils used in the current study. The different methanol to oil ratios optimized for various oils depends upon the viscosity of the oil as well as the viscosity of the oil/methanol mixture formed after the addition of the catalyst. Castor oil is already known to have a higher viscosity than many other vegetable oils [35]. Thus, high amounts of methanol are required for the proper conversion of the reactant to biodiesel [36].

A longer separation time was required for the separation of the biodiesel from the water layer for a high molar ratio. This is due to the fact that the one hydroxyl group present in the methanol can work as an emulsifier to increase emulsion. Therefore, increasing the molar ratio of methanol to oil beyond 5:1 (in the case of wild mustard and wild safflower),

10:1 (in the case of karanja and bitter apple) and 15:1 (in the case of castor oil) was not suitable for increasing the biodiesel yield, but it made the recovery of ester difficult and increased the methanol recovery cost [36]. In addition to the already described viscosity factor, the variations in the FFA and water contents in the different types of oil also play a vital role in the optimization of the methanol to oil ratio. The variation in the FFA contents of some plant oils causes the used catalyst to react differently towards the different oils [37].

2.6.3. Effect of Temperature

Transesterification can be conducted at temperatures from room temperature to a temperature that is close to methanol's boiling point. However, transesterification reactions generally occur at high speed at elevated temperatures with shortened reaction periods. The importance of the reaction temperature in the transesterification of oils can be clearly observed from the much-boosted yields obtained in the present study after elevating reaction temperature. To study the effect of temperature on ester content and the yield of the transesterification, experiments were conducted at 40–80 °C by keeping the volume and other reaction variables constant. It is clear from the results shown in Tables 3–7 that the increase in the reaction temperature increases biodiesel yield. The increase in temperature accelerated the transesterification reaction, not only by decreasing viscosity but also by increasing mass transfer and initiating the more effective collision between molecules participating in the chemical reaction [36]. In the present study, karanja, bitter apple, wild mustard, and wild safflower oils showed the highest biodiesel yield at 50 °C, while castor oil provided the highest biodiesel yield at 60 °C. The higher optimized temperature to produce biodiesel from castor oil can be related to the higher viscosity of castor oil than other oils. Higher temperature could lead to a decrease in the viscosity of castor oil, making the reaction between oil and methanol molecules more favorable for the more effective conversion of triglycerides. The rise in temperature also favors the relative miscibility of the non-polar oil phase to polar alcoholic media to increase the speed of the chemical reaction [38]. However, increasing the temperature beyond the optimized temperature resulted in a decreased biodiesel yield due to the greater possibility of side reactions that can take place at higher temperatures along with a higher loss of methanol from the reaction mixture due to greater evaporation [39].

2.6.4. Reaction Time

The transesterification reaction is an equilibrium reaction, and the reaction time is a crucial variable to obtain the maximum biodiesel yield in an optimized reaction period. If a too-short reaction time is selected, there will not be complete conversion of reactants into products and the purification cost will also be higher. On the other hand, if a too-long reaction time is selected, there will be higher production cost and the product could also undergo decomposition or side reactions. To determine the optimum reaction time to produce biodiesel from oils (bitter apple; karanja; wild mustard; castor; and wild safflower oils), the reactions were performed at different reaction times (30 to 150 min) for the 20% Li-TiO_2/feldspar catalyst. The impact of time on the transesterification reactions performed on the different oil samples is presented in Tables 3–7.

The bitter apple, karanja, castor, and wild safflower oils provided the maximum methyl ester yield after 120 min. The highest biodiesel yield for bitter apple, karanja, castor, and wild safflower oils was 96.2 ± 0.8%, 96.4 ± 0.9%, 96.1 ± 0.3%, and 96.5 ± 0.3%, respectively, while the wild mustard oil provided the best biodiesel yield of 96.7 ± 0.7% after 90 min. Transesterification reaction is an equilibrium reaction, and there is always the possibility of a reverse reaction if reaction times are longer. Longer time periods are required for oils with higher saturated fatty acid contents [37–48].

2.7. Evaluation of Fuel Quality Parameters

The structural features of each fatty ester present in the fatty acid methyl esters determine its physicochemical properties such as density, acid value, iodine value, saponification

value, cold flow properties (cloud and pour points) and ignition quality. The fuel characteristics of the alkyl esters synthesized from bitter apple, karanja, wild mustard, castor and wild safflower were evaluated according to ASTM (D6751) standard methods and compared with diesel (Table 8). This standard identifies the parameters that the pure biodiesel must meet before being used. Density is a very important fuel property because the precise fuel amount is required for proper combustion. High-density biodiesel could experience incomplete combustion, while on the other hand, low-density biodiesel fuels are highly volatile. The densities of biofuels depend on the feedstock's nature, the biodiesel's synthesis method and the structural features of methyl ester [40]. The densities of biodiesel produced from bitter apple, karanja, wild mustard, castor and safflower oils were 0.85, 0.89, 0.84, 0.87 and 0.86 g/mL, respectively.

Table 8. Fuel properties of FAME produced from various sources.

Fuel Parameters	Bitter Apple	Karanja	Wild Mustard	Castor Oil	Wild Safflower	Diesel ASTM D975	ASTM D6751 Limits
Density (g/mL)	0.85	0.89	0.84	0.87	0.86	0.85	Not specified
Cloud point (°C)	1.3	2.0	−2	1.2	0.2	−15–5	−15 to 10
Pour point (°C)	−4.2	−1.6	−4.2	−4.1	−4.0	−35–15	Not specified
Acid value (mg KOH/g)	0.43	0.17	0.43	0.27	0.41	-	0.50 max
Iodine value (g I_2/100 g)	96.31	85.1	76.77	86.04	78.64	-	Not specified
Saponification value (mg KOH g^{-1} oil)	190.92	176.03	185.05	187.01	179.74	-	Not specified
Cetene number	53.21	58.15	58.52	56.12	58.97	40–55	47 minimum

An important criterion to determine a biofuel's quality is the fuel's low temperature behavior, as it could solidify in filters and pipelines of the engine and may cause different problems such as fuel undernourishment and delayed ignition. The cloud point (CP) is the temperature at which it appears hazy or cloudy. The pour point (PP) is the temperature at which the lubricating oil ceases to flow [41]. From the obtained results, it was observed that the cloud and pour points measured for the produced FAME from bitter apple, karanja, wild mustard, castor and wild safflower oils using the 20% Li-TiO_2/feldspar nanocatalyst lie in the range which was prescribed by the ASTM.

The acid value (AV) is the amount of potassium hydroxide (in milligrams) required for the neutralization of the organic acids per gram of fat [42]. The AVs of the synthesized biodiesels from bitter apple, karanja, wild mustard, castor, and wild safflower oils in the presence of the 20% Li-TiO_2/feldspar catalyst were 0.43, 0.17, 0.43, 0.27 and 0.41 mg KOH g^{-1}, respectively (Table 8). The iodine value (IV) is measured as the amount of iodine (in grams) that is adsorbed by 100 g of oil or biodiesel [43]. The iodine values of the biodiesels synthesized from bitter apple, karanja, wild mustard, castor and wild safflower oils were 96.31, 85.1, 76.77, 86.04, and 78.64 g I_2/100 g, respectively.

The conversion of fat/oil/lipid by means of a reaction with aqueous alkali into alcohol and soap is called the saponification reaction [42]. The saponification values of the biodiesels produced from bitter apple, karanja, wild mustard, castor and wild safflower oils were 190.92, 176.03, 185.05, 187.01 and 179.74, respectively. The cetane number (CN) reflects the ignition delay period [41]. The cetene numbers of the biodiesels produced from bitter apple, karanja, wild mustard, castor and wild safflower oils were 53.21, 58.15, 58.52, 56.12, and 58.97, respectively.

2.8. Fatty Acid Profile

A biodiesel is a mixture of long-chain FAs, with the number of C atoms present in the chain varying from 14 to 22 [44]. The main fatty acids appearing in bitter apple [48],

karanja [45], wild mustard, castor [47], and wild safflower [46] oils were linoleic acid (70.71%), oleic acid (51.92%), erucic acid (41.43%), ricinoleic acid (80.54%), and linoleic acid (75.17%), respectively (Table 9).

Table 9. The chemical composition of used oils.

Sr.No.	Fatty Acid	Molecular Formula	Fatty Acid Amount (%)				
			Karanja Oil	Wild Mustard Oil	Wild Safflower Oil	Castor Oil	Bitter Apple Oil
1	Capric acid	$C_{10}H_{20}O_2$	0.11	0.15	0.13	0.12	0.07
2	Lauric acid	$C_{12}H_{24}O_2$	0.22	0.12	0.09	0.08	0.06
3	Myristic acid	$C_{14}H_{28}O_2$	0.93	0.18	0.16	0.11	0.13
4	Palmitic acid	$C_{16}H_{32}O_2$	10.33	3.63	7.73	1.30	8.35
5	Margaric acid	$C_{17}H_{34}O_2$	0.09	0.05	0.06	0.07	0.01
6	Linolenic acid	$C_{18}H_{30}O_2$	3.15	0.09	0.32	1.57	0.17
7	Linoleic acid	$C_{18}H_{32}O_2$	11.03	15.75	75.17	7.65	70.71
8	Oleic acid	$C_{18}H_{34}O_2$	51.92	23.11	12.98	5.83	9.96
9	Ricinoleic acid	$C_{18}H_{34}O_3$	-	-	-	80.54	0
10	Stearic acid	$C_{18}H_{36}O_2$	4.66	1.15	0.89	1.43	8.29
11	Eicosanoic acid	$C_{20}H_{40}O_2$	9.76	12.83	0.11	0.18	0.03
12	Arachidic acid	$C_{20}H_{40}O_2$	0.96	0.07	0.76	0.21	0.11
13	Erucic acid	$C_{22}H_{42}O_2$	-	41.43	-	-	0.17
14	Behenic acid	$C_{22}H_{44}O_2$	4.36	0.09	0.43	0.17	0.07
15	Lignoceric acid	$C_{24}H_{48}O_2$	2.12	1.12	0.32	0.15	1.13

3. Materials and Methods

3.1. Chemicals and Reagents

Analytical grade methanol (99%), Wijs reagent, ethanol (99.5%), titanium dioxide, lithium nitrate, sodium sulphate (anhydrous), hydrochloric acid (37%), potassium hydroxide, sodium hydroxide (98%), petroleum ether, starch, Wijs solution, sodium thiosulphate, phenolphthalein, and potassium iodide were purchased from Sigma-Aldrich (Lahore, Pakistan).

3.2. Materials and Oil Extraction

Citrullus colocynthis (bitter apple), *Pongamia pinnata* (karanja), *Sinapis arvensis* (wild mustard), *Ricinus communis* (castor oil) and *Carthamus oxyacantha* (wild safflower) seeds were collected after obtaining permission from Head of Department (HOD,) Department of Chemistry, UAF, Pakistan. The plant materials, including bitter apple, karanja, wild mustard, castor and wild safflower, were identified by Dr. Mansoor Hameed, UAF, and the sample voucher specimen numbers were 21-R-001, 21-R-002, 21-R-003, 21-R-004 and 21-R-005, respectively. All of the experimental research and field studies on plants were conducted in compliance with the standard rules. After the sample collection, seeds were cleaned to remove all of the foreign particles, such as dirt, chaff, stones, dust, and immature broken seeds. Seeds were extracted from kernels. Extracted seeds were crushed and ground with the help of a pestle and mortar. Oil was extracted using an automatic screw press machine. The screw press machine compressed the seeds between the main screw and travelling cones for the extraction of oil from the seeds. This machine separated the oil and non-oily solid (cake). The extracted oil was further purified using a high-speed centrifuge at 5000 rpm followed by filtration with a vacuum filtration assembly. By using the vacuum filtration assembly, the oil was filtered off to remove impurities and solid particles.

3.3. Catalyst Preparation

The Li-incorporated TiO_2 nano-catalysts were synthesized via a wet impregnation process. We took 10 g of TiO_2 nanoparticles and dissolved them in 20 mL of distilled water and heated this solution at room temperature with slow stirring. Subsequently, the desired concentration of lithium nitrate was added dropwise. Additionally, the resultant slurry was mixed for 4 h at room temperature using a thermostatic magnetic stirrer and heated overnight in an oven at 120 °C, and the obtained sample was calcined at 600 °C in a muffle furnace for 4 h. Similarly, a series of Li-impregnated TiO_2 nanoparticles with different amounts of Li (10, 20, 30 and 40 wt%) were synthesized.

In order to resolve the problem faced by using a catalyst without a support for the production of biodiesel, the clay mineral feldspar was used to prepare the supported catalysts in the present study. The nano-catalysts of Li-TiO_2 with different amounts of Li (10%, 20%, 30%, 40%) were supported on feldspar. For the synthesis of supported catalysts, 0.5 g of each prepared nanocatalyst and 0.75 g of feldspar support were dissolved into distilled water to create a uniform paste. The mixture was then dried in an oven at 150 °C for half an hour to eliminate the moisture. The prepared supported nano-catalysts were ground with the help of a pestle and mortar. A nano-sieve was used to separate the nanoparticles from bigger particles.

3.4. Characterization

X-ray diffraction was performed to determine the nanocatalysts' structure by using a Shimadzu model 6000 Power X-ray diffractometer (Shimadzu Corp., Kypoto, Japan). The obtained diffraction peaks were compared with standard compounds described in the Joint Committee on Powder Diffraction Standards (JCPDS) databank. The average crystal size of Li-TiO_2/feldspar was determined using the Debye–Scherrer equation.

FTIR (Agilent technologies, Santa Clara, CA, USA) analysis was carried out to identify the functional groups present in Li-TiO_2/feldspar nanocatalysts. The morphological structure and elemental composition of nanoparticles were determined using SEM (NOVA NANOSEM-450, Thermo Fisher Scientific, New York, NY, USA) and EDX (Nova 450), respectively. The fatty acid composition of oils was determined by means of gas chromatography equipped with a flame ionization detector.

3.5. Transesterification Process

In the presence of nanocatalysts, biodiesel was produced by means of transesterification of bitter apple, karanja, wild mustard, castor, and wild safflower oils using methanol. Several reversible and successive steps are involved in transesterification. Biodiesel is the major product of the reaction and floats on top, while the by-product glycerol is present at the bottom. Different concentrations of lithium (10–40% Li/TiO_2)-doped titanium oxide nanocatalysts supported on feldspar were used for transesterification.

The methanol to oil molar ratio (5:1, 10:1, 15:1, 20:1 and 25:1), catalyst amount (0.5%, 1%, 1.5%, 2% and 2.5%), reaction temperature (40; 50; 60, 70; and 80 °C), and reaction time (30, 60, 90, 120 and 150 min) were optimized during the present study to obtain the maximum biodiesel yield. After the completion of the reaction, the prepared biodiesel was centrifuged at 1500 rpm for 20 min for the removal of the remaining nanocatalysts from the biodiesel. Hot distilled water in an excess amount was used to wash the produced biodiesel and to remove surplus methanol from the biodiesel. The cleared transparent liquid was obtained after proper washing of the biodiesel. The biodiesel % yield was calculated by applying Equation (2).

$$Process\ yield\ (\%) = \frac{Pure\ biodiesel\ (g)}{Oil\ used\ (g)} \times 100 \quad (2)$$

3.6. Quality Parameters of Biodiesel

The biodiesel quality parameters such as density, acid value, pour point (PP), iodine value (IV), cetane number (CN), saponification value (SV), and cloud point (CP) were determined using methods and equations given in the literature [6].

4. Conclusions

The aim of the present research was to compare the yield of biodiesel from different non-edible oils such as *Citrullus colocynthis* (bitter apple), *Pongamia pinnata* (karanja); *Sinapis arvensis* (wild mustard), *Ricinus communis* (castor oil), and *Carthamus oxyacantha* (wild safflower) using a novel lithium-impregnated titanium oxide catalyst supported on feldspar minerals (Li-TiO_2/feldspar) and to assess the efficiency of the synthesized nanocatalysts under mild reaction conditions. A series of lithium-impregnated titanium oxide nanocatalysts with different amounts of Li (10%, 20%, 30%, 40%) supported on the clay mineral feldspar (Li-TiO_2/feldspar) were investigated, conducting the transesterification process for biodiesel production. However, the study showed that 20 wt% of Li showed the highest activity for FAME formation. The characterization of support-loaded catalysts was performed using XRD, SEM/EDX and FTIR analysis. The major fatty acids present in bitter apple, karanja, wild mustard, castor, and wild safflower oils were linoleic acid (70.71%), oleic acid (51.92%), erucic acid (41.43%), ricinoleic acid (80.54%), and linoleic acid (75.17%), respectively. One of the aims of the present study was to look for a universal transesterification catalyst that could effectively convert feedstock oils of quite variable compositions with good efficiency, and the produced Li-TiO_2/feldspar is found to be such a catalyst.

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