

## Research Article

# Preparation and Characterization of Alkaline and Acidic Heterogeneous Carbon-Based Catalysts and Their Application in Vegetable Oil Transesterification to Obtain Biodiesel

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This paper reports the preparation, evaluation, and comparison of alkaline and acidic heterogeneous carbon-based catalysts in the transesterification of safflower oil with methanol to obtain biodiesel. These catalysts were obtained from the pyrolysis of flamboyant pods and their functionalization and activation with potassium hydroxide, citric acid, tartaric acid, sulfuric acid, and calcium nitrate. Different routes for the preparation of these catalysts were tested and analyzed where the FAME formation was the target variable to be improved. Results showed that the catalyst prepared with potassium hydroxide and calcium nitrate achieved the highest FAME formation (i.e., 95%) and outperformed the catalysts prepared with calcium nitrate and other acids even after four regeneration-reaction cycles. The best properties of an alkaline catalyst could be associated with its specific surface area and contents of potassium and calcium moieties, which were higher than those observed for acidic catalysts. Transesterification rates for biodiesel production were better estimated with the pseudo-order kinetic model, which ranged from 0.0004 to 0.038 L/mol-min for alkaline and acidic catalysts.

## 1. Introduction

Transesterification has a variety of industrial applications including, the production of solvents and additives like diethyl and dipropyl carbonate [1–3], flavonoid derivatives to improve the physicochemical characteristics of food and pharmaceutical products [4, 5], and n-butyl acetate that can be used in the processing of resins, plastics, coatings, and gums [6]. This reaction is also commonly utilized to obtain biodiesel, which has been considered an alternative and environmentally friendly fuel [7, 8]. Biodiesel can be produced from the reaction of biomass oils (e.g., corn, sorghum, cassava, and sugarcane), comestible vegetable oils (e.g., rapeseed, soybean, and palm oils), nonedible vegetable oils (e.g., *Jatropha curcas*, karanja, and neem oils), and lipids

contained in sludge from wastewater treatment plants, animal fats, waste cooking oils, and microalgae lipids [9–11].

This reaction is thermodynamically reversible where essentially an alkyl group of an ester is mixed with monohydric aliphatic alcohol such as methanol or ethanol. It is also called alcoholysis or acidolysis (if the ester reacts with carboxylic acid to substitute the alkyl group with the acid). Both schemes can occur in the presence of a catalyst to generate another ester (biodiesel) and glycerol that can be also commercialized as a high-value coproduct [12, 13].

The catalysts used in this reactive system are fundamental to achieve a proper conversion extent, and consequently, the selection of the best catalyst is a crucial step to get the optimal reaction conditions and to reduce the cost of final products [14–16]. These catalysts can be classified as

homogeneous or heterogeneous [17]. In particular, heterogeneous catalysts have increased their industrial applications because they offer some advantages with respect to homogeneous catalysts such as the elimination of the washing step of the final products, easy regeneration, less corrosive, and low-cost [18, 19]. Heterogeneous catalysts can be classified as basic, acidic, and enzymatic [20]. In the case of biodiesel production, acidic and alkaline catalysts are preferred to enzymatic catalysts since their cost is lower and also offer a better catalytic performance; besides, enzyme-based catalysts can be easily deactivated [21–23]. Acidic and alkaline heterogeneous catalysts have been utilized and analyzed [22–26], and results showed that catalyst selection mainly depends on the nature of the reacting oil. If the amount of free fatty acids (FFA) in the oil is low, alkaline catalysts are recommended because they can promote the highest conversion [27]. Note that acidic heterogeneous catalysts are more suitable for oils with high FFA content [28]. Alkaline heterogeneous catalysts are considered non-corrosive, environmentally friendly, and recyclable, and they also provide appropriate selectivity and long lifetime. Nevertheless, their main drawbacks are that they require oils with low FFA and water content and a high ratio of methanol to oil besides high pressure and temperature as reaction conditions [21, 23]. Alternatively, acidic heterogeneous catalysts are insensitive to water and FFA content in the oil, and they are preferred for processing low-grade oils where esterification and transesterification can occur at the same time. Some authors have indicated that the cost of these catalysts can increase due to their complicated synthesis procedures. However, these catalysts are more sensitive to the reaction conditions and may also require a high reaction temperature, long reaction time, and high alcohol to oil molar ratio, and the leaching of catalyst active sites could generate environmental pollution [22, 23, 29–31].

Heterogeneous catalysts can be prepared by employing different supports. Recent studies and advances in the preparation of heterogeneous catalysts for biodiesel production include catalysts with magnetic properties, composites functionalized with multivalent species, and ionic liquids besides the application of novel materials like metal-organic frameworks [17, 18, 27, 32, 33]. In this direction, carbon-based materials are an alternative to consolidate and intensify the production of several chemicals including biodiesel [29, 31, 34–36]. These carbon-based catalytic supports can be obtained from forest biomass and agricultural and urban wastes. Therefore, they are considered low-cost supports in comparison with other materials (e.g., silica, alumina, and ion-exchange resins); besides, they can operate in a wide spectrum of conditions including high temperature and pressure and acidic or basic media [30, 37]. Carbon-based supports show an acid-base character because of the presence of oxygenated functionalities that also allow the incorporation of metallic species on the catalyst surface to improve their activity [17, 38]. The surface properties of carbon-based supports can be modified with different protocols to achieve a target catalytic performance. For instance, one option to improve the active component dispersion on the support surface implies functionalization

with an acidic or basic treatment or oxidization with  $\text{CO}_2$  or steam to add specific functional groups [38]. These added functionalities can act as anchoring sites during the incorporation of catalytic species [39]. Bases, acids, or oxides (e.g.,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_2\text{O}_2$ ) can be employed to provide basic or acidic properties on the supports [40].

To date, several studies have reported the preparation, functionalization, and application of carbon-based catalysts in biodiesel production [12, 35, 36, 41–44]. For example, Devi et al. [43] described the synthesis of a glycerol-based carbon catalyst. This catalyst was prepared from the partial carbonization of glycerol, a sulfonation step with  $\text{H}_2\text{SO}_4$ , and a treatment with a solution of 20%  $\text{NaOH}$  at  $90^\circ\text{C}$  for 2 h. This catalyst was tested to obtain biodiesel from safflower oil and methanol. The transesterification conditions of this study were as follows: an oil to methanol ratio of 1 : 1 to 1 : 5, a catalyst dosage of 5 to 20 wt%, and a reaction time of 2 to 15 h at  $65^\circ\text{C}$ . Conversion up to 99% was obtained with 2 h of reaction, 1 : 5 methanol (wt/v) at a reflux temperature of  $65^\circ\text{C}$  with 20 wt% of the catalyst. Zhao et al. [44] evaluated a pomelo seed-based catalyst to produce biodiesel. Pomelo seed was pyrolyzed under an  $\text{N}_2$  atmosphere at  $600^\circ\text{C}$  for 2 h. This char was mixed with a solution of 2 M  $\text{KOH}$  for 2 h, and a wet impregnation method with  $\text{K}_2\text{CO}_3$  solution was employed in its modification. The final catalyst showed a biodiesel yield of 98% via the transesterification of palm oil with methanol at  $65^\circ\text{C}$ . Other examples of carbon-based heterogeneous catalysts utilized to produce biodiesel have been reported by Jamil et al. [35], Faria et al. [45], Cao et al. [46], Leesing et al. [47], and Rokhum et al. [48]. Results of these studies have provided enough evidence to conclude that the preparation of carbon-based materials is an attractive and alternative approach to obtain low-cost and eco-friendly catalysts for the production of biodiesel and other relevant chemicals. However, few studies have performed a detailed comparison of the capabilities and limitations of both acidic and alkaline heterogeneous carbon-based catalysts for biodiesel production, where the chosen preparation route is paramount. In particular, the analysis of surface activation and functionalization of alkaline and acidic heterogeneous catalysts is required to consolidate the application of these materials in the production of biofuels.

This manuscript reports the preparation, functionalization, evaluation, and comparison of flamboyant pods-based catalysts to obtain a biofuel. These carbon-based materials have been treated and functionalized with different acids (tartaric, citric, and sulfuric acid), a base (potassium hydroxide), and calcium nitrate to obtain a set of acidic and alkaline heterogeneous catalysts for biodiesel production. Catalytic and surface properties of the materials prepared with different routes have been analyzed and compared in vegetable oil transesterification under the same operating conditions. The best catalyst was selected to study the thermodynamic and kinetic parameters of transesterification of methanol and safflower oil to produce this biofuel. In summary, the main contribution of this study relies on the comparison of capabilities and limitations of different carbon-based heterogeneous catalysts functionalized with  $\text{KOH}$  and calcium for oil transesterification to obtain biofuels.

## 2. Methodology

**2.1. Preparation of Acidic and Alkaline Heterogeneous Catalysts.** Flamboyant pods (FP) were used as the biomass to prepare the acidic and alkaline heterogeneous catalyst for biodiesel production. This biomass was collected in Colima (Mexico), and it was milled, washed, dried, and sieved to obtain an average particle diameter of 0.105 mm. A set of alkaline and acidic catalysts was prepared with this biomass where the Taguchi  $L_9$  experimental design was utilized to identify the best synthesis conditions to maximize the performance of these catalysts in the vegetable oil transesterification to obtain biodiesel. Table 1 shows the experimental design employed in the preparation of these catalysts, and Figure 1 describes the steps performed for their functionalization and activation.

First, the carbon-based supports were prepared via the pyrolysis of FP biomass at 600°C for 2–4 h with a heating rate of 10°C/min under  $N_2$  atmosphere (200 mL/min). Biomass pyrolysis was performed to obtain the carbon-based supports (i.e., chars) with a tubular furnace Carbolite Eurotherm CTF 12165/550 using a quartz sample holder that was loaded with 30 g of an FP precursor. 1 g of these chars was functionalized with 25 mL of tartaric (TA), citric (CA), sulfuric (SA) acid, and potassium hydroxide (K) using different concentrations (0.5–2 M) at room temperature for 5 h. These functionalized chars were heated at 150°C for 1–4 h and were washed and dried at 110°C for 24 h. A solution of  $Ca(NO_3)_2$  with different concentrations (0.1–0.3 M) was employed to treat these samples for 5 h at room temperature. Finally, these materials were activated at 700°C for 2 h under  $N_2$  flow of 200 mL/min. All catalysts were rinsed with deionized water and dried at 110°C for 24 h. A total of 9 catalyst samples were obtained from each functionalization protocol (i.e., a total of 36 catalyst samples were prepared and tested). The results of the experimental designs allowed us to identify the impact of biomass pyrolysis, functionalization, and activation conditions on the properties of these heterogeneous catalysts. The formation percentage of fatty acid methyl esters (FAME) obtained via the transesterification of vegetable oil with methanol was the variable to be improved in this experimental design.

Surface chemistry properties of selected carbon-based supports and catalysts were analyzed to explain their catalytic performance. The crystallinity and structural phase of the samples were determined by X-ray diffraction, and elemental analysis was performed by X-ray fluorescence spectrometry (XRF) by dispersive energy. Surface functional groups were identified via FTIR spectra recorded with the Thermo Scientific Nicolet iS10 FTIR spectrophotometer. Main textural properties were determined with  $N_2$  physisorption at  $-196^\circ\text{C}$ . SEM/EDS analysis was carried out to determine the morphology and surface elemental composition. Details of these characterization techniques are provided in Supporting Information.

**2.2. Assessment of Heterogeneous Catalysts in the Vegetable Oil Transesterification for Biodiesel Production.** The catalytic properties of supports, acidic, and alkaline carbon-based

materials were assessed and compared in the transesterification of commercial safflower oil and methanol to obtain biodiesel under batch conditions. The performance of supports (i.e., chars obtained from biomass pyrolysis without functionalization and activation) was the basic line to compare and analyze the protocols used to tailor the properties of heterogeneous catalysts. The transesterification conditions were as follows: 5 wt% of the catalyst with respect to the vegetable oil and methanol to vegetable oil ratio of 15:1 at 60°C for 5 h under continuous stirring at 600 rpm. After the reaction, the catalyst was separated from the liquid phase via centrifugation. Residual methanol was evaporated from the remaining solution, and the FAME content was quantified in the final upper phase via gas chromatography using Thermo Scientific Trace 1300 GC. Details of the equipment operating conditions are given in Supporting Information. Methyl heptadecanoate was employed as an internal standard to determine the FAME content (wt%) by following the approach reported by Chen et al. [49] and di Bitonto et al. [50].

A statistical analysis of the results obtained from the experimental design of Table 1 was performed to assess the different approaches to prepare heterogeneous catalysts. This statistical analysis was carried out with the signal-to-noise ratio (S/N) that was defined using the ratio of FAME contents ( $R_{FAME}$ ) obtained from the catalysts and their corresponding supports

$$\frac{S}{N} = -10 \log \left( \frac{1}{n_{rep}} \sum_{i=1}^{n_{rep}} \left[ \frac{1}{x_i^2} \right] \right), \quad (1)$$

$$x_i = R_{FAME} = \frac{\text{FAME percentage using catalyst}}{\text{FAME percentage using support}}$$

where  $n_{rep} = 2$  is the number of experimental replicates of vegetable oil transesterification to obtain biodiesel. Overall,  $R_{FAME} > 1$  indicates that the catalyst outperforms the activity of its carbon-based support (i.e., char). The best conditions to prepare the catalysts with the highest FAME formation were identified via the analysis of the S/N ratio where the target was to maximize this metric (i.e.,  $\uparrow$  S/N,  $\uparrow$   $R_{FAME}$ ). ANOVA of all the experimental designs was conducted according to the equations reported in the Supporting Information.

### 2.3. Kinetics and Modeling of Vegetable Oil Transesterification to Obtain Biodiesel Using the Best Heterogeneous Catalyst.

The reaction temperature is an important parameter in vegetable oil transesterification to obtain biodiesel. Therefore, the impact of this parameter was tested using the best heterogeneous catalyst identified with the experimental designs. Oil transesterification was performed at 50, 60, and 80°C, and the reaction kinetic profile was determined from 0.5 to 8 h under continuous stirring at 600 rpm. Note that the remaining experimental conditions were similar to those applied for testing the catalysts obtained from the experimental designs. The profiles of FAME formation were employed to calculate the reaction rates and thermodynamic parameters. Transesterification rates were calculated with a

TABLE 1: Taguchi  $L_9$  experimental design used for the preparation of alkaline and acidic heterogeneous catalysts from flamboyant pods.

Catalyst sample	Time of biomass pyrolysis (h)	Concentration of acid or alkaline solution (M)	Time of thermal treatment at 150°C (h)	Calcium salt concentration (M)
1	2	0.5	1	0.1
2	2	1.0	2	0.2
3	2	2.0	4	0.3
4	3	0.5	2	0.3
5	3	1.0	4	0.1
6	3	2.0	1	0.2
7	4	0.5	4	0.2
8	4	1.0	1	0.3
9	4	2.0	2	0.1

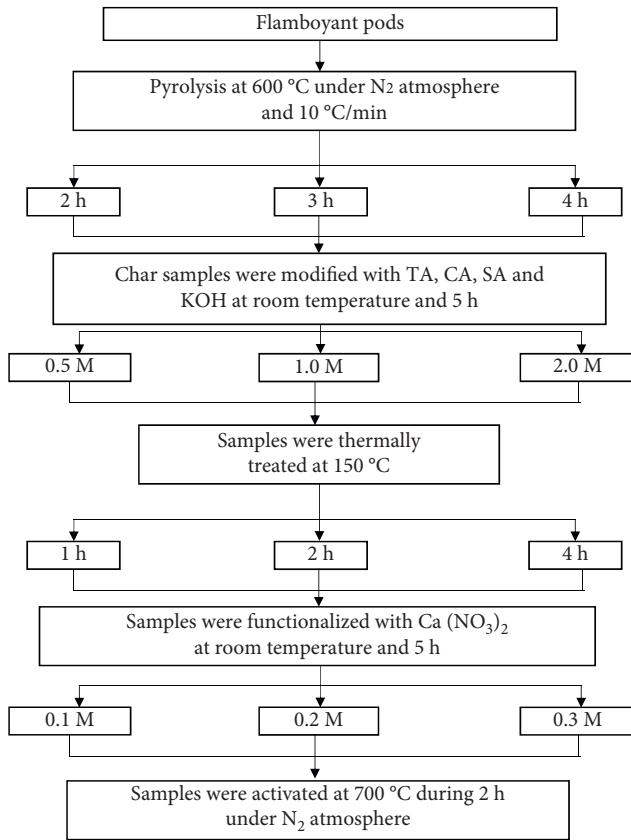


FIGURE 1: Main steps involved in the functionalization and activation of acidic and alkaline heterogeneous catalysts for obtaining biodiesel via vegetable oil transesterification.

lumping approach assuming that FAME were obtained from the reaction of triglycerides (i.e., 85 wt% of total glycerides) of safflower oil [51]. The next kinetic equations were applied in the following analysis [52]:

$$-\ln(1 - X_{ME}) = k_1 t, \quad (2)$$

$$\frac{X_{ME}}{1 - X_{ME}} = k_2 C_{MeO} C_{OH0} t,$$

where  $t$  (min) is the transesterification time,  $X_{ME}$  is the triglyceride conversion,  $C_{MeO}$  and  $C_{OH0}$  are the initial concentrations of triglyceride and methanol (mol/L), respectively,  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2 = k' C_{MeO} C_{OH0}$  ( $\text{L/mol}\cdot\text{min}$ ) are

the transesterification rate constants. A linear regression of the Arrhenius equation was utilized to estimate the activation energy ( $E_a$ , kJ/mol) of vegetable oil transesterification to obtain biodiesel as shown in the following equation:

$$\ln k = \ln A - \frac{E_a}{RT}, \quad (3)$$

$$k = A e^{-(E_a/RT)},$$

where  $T$  (K) is the transesterification temperature,  $R$  (J/mol·K) is the ideal gas constant, and  $A$  is the frequency factor, respectively.

**2.4. Catalyst Regeneration and Reuse.** The activity of heterogeneous catalysts was analyzed after several reaction cycles. In these experiments, 2 g of the catalyst was utilized where the oil transesterification conditions were the same as those reported in the previous section (i.e., 15:1 methanol to vegetable oil molar ratio, 60°C, 5 h, and 600 rpm). The catalyst regeneration was performed with 50 mL of methanol at 40°C for 2 h. The regenerated catalysts were dried at 100°C for 24 h and assessed in other reaction cycles. This procedure was repeated several times until the catalytic activity reached its minimum value.

### 3. Results and Discussion

**3.1. Analysis of Preparation Conditions of Heterogeneous Catalysts and Their Evaluation in Oil Transesterification.** The results of transesterification to obtain biodiesel with the set of 36 acidic and alkaline heterogeneous catalysts are shown in Figure 2. Overall, the yields of catalyst preparation were 87.2–91.7%, 90.6–98.5%, 75.5–85.2%, and 74.7–83.7% for the samples obtained with CA, TA, SA, and K, respectively. These catalysts showed percentages of FAME formation that ranged from 22.16 to 25.06% for CA, 20.89 to 24.25% for TA, 21.02 to 27.96% for SA, and 46.94 to 95.64% for K, respectively. All acidic catalysts were outperformed by their alkaline counterparts prepared under the same experimental conditions. In general, catalyst sample No. 3 of each preparation route (which was obtained with 2 M concentration of acidic or alkaline solution for 2 h plus 4 h of thermal treatment at 150°C and finally functionalized with 0.3 M calcium salt concentration and activated at 700°C for 2 h) showed the best performance to produce biodiesel. The highest FAME

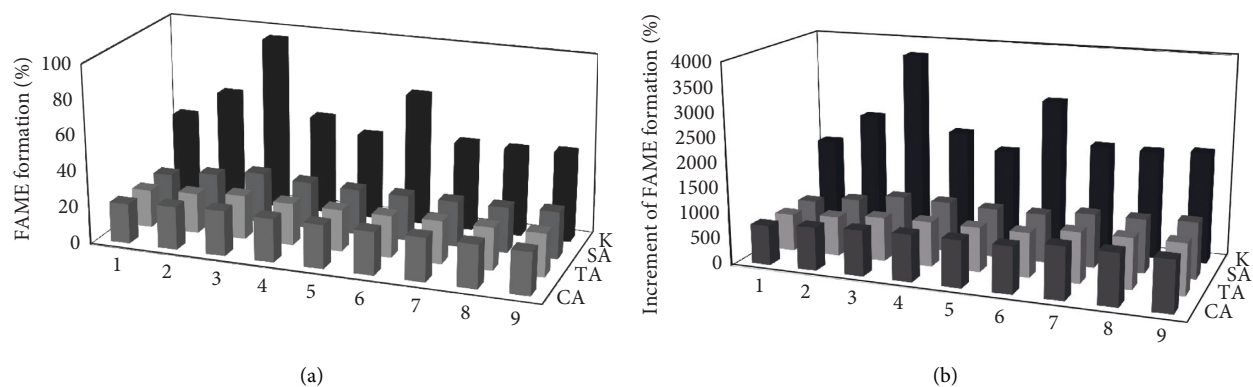


FIGURE 2: (a) FAME formation of acidic and alkaline heterogeneous catalysts and (b) increment of catalytic properties with respect to the corresponding carbon-based supports.

formation obtained with these catalysts was 25.06, 24.25, 27.96, and 95.64% for 3CA, 3TA, 3SA, and 3K samples, respectively. On the other hand, all the supports achieved FAME formation of  $\sim 3\%$  regardless of the dwell time employed in the biomass pyrolysis. Figure 2(b) shows a comparison of the increment of catalytic properties of all the samples after the support functionalization and activation. Specifically, the increment of FAME formation of the catalysts with respect to the corresponding carbon-based supports was up to 1031, 1012, 1114, and 3726% for 3CA, 3TA, 3SA, and 3K samples, respectively. These results clearly indicated that the surface functionalization and activation procedures had a remarkable influence on the final catalyst properties.

In particular, flamboyant pods-based supports functionalized and activated with KOH showed the best catalytic properties. This result corroborated the fact that the catalysts with a basic nature usually have higher catalytic activity in transesterification for a feedstock with low FFA like commercial safflower oil [21, 25, 29, 35]. Acidic catalysts can improve their performance to produce FAME if more severe reaction conditions are employed (e.g., high reaction temperature, high alcohol to oil molar ratio, and long reaction time) [53]. In summary, the catalytic activity of these samples in the transesterification of commercial safflower oil with methanol to obtain biodiesel was as follows:  $K \gg SA > CA > TA$ .

Figure 3 shows the S/N ratio analysis for the variables studied in the catalyst preparation with tested acidic and alkaline solutions. In general, the catalytic properties of these materials improved with the acidic or alkaline concentration, thermal treatment time during the functionalization step, and calcium salt concentration. In the case of biomass pyrolysis, the catalytic properties of samples obtained with citric acid and potassium hydroxide were better with a pyrolysis dwell time of 2 h, while 4 h of biomass pyrolysis favored the performance of catalysts prepared with tartaric acid and sulfuric acid. ANOVA analysis showed the next trends for the impact of preparation conditions on catalyst performance which are as follows:

Citric acid-based catalyst samples: time of thermal treatment at  $150^\circ\text{C} \cong$  calcium salt concentration  $>$  citric acid concentration  $>$  time of biomass pyrolysis

Sulfuric acid-based catalyst samples: time of thermal treatment at  $150^\circ\text{C} >$  calcium salt concentration  $\cong$  sulfuric acid concentration  $>$  time of biomass pyrolysis

Tartaric acid-based catalyst samples: tartaric acid concentration  $>$  time of thermal treatment at  $150^\circ\text{C} \cong$  calcium salt concentration  $>$  time of biomass pyrolysis

Potassium hydroxide-based catalyst samples: potassium hydroxide concentration  $>$  time of biomass pyrolysis  $\cong$  calcium salt concentration  $>$  time of thermal treatment at  $150^\circ\text{C}$

Table S1 of Supporting Information provides the results of ANOVA for tested experimental designs. For the case of the alkaline catalysts, KOH concentration was the most relevant variable that impacted the properties of these materials to obtain biodiesel via transesterification. Similar findings were reported by Agarwal et al. [19] and Saba et al. [54] where the increment of KOH impregnation on alumina and ZSM5 zeolite increased the FAME content. This result was attributed to the high active phase loading on the solid. It is also important to note that the presence of potassium-based functionalities loaded on several solids has been directly related to catalytic activity in oil transesterification [55–58].

Figure 4 shows the X-ray diffraction patterns of the selected catalyst samples and the carbon-based support. The samples of catalysts obtained with tartaric acid, sulfuric acid, and potassium hydroxide showed diffraction patterns with two wide peaks at  $\sim 23$  and  $\sim 43$   $2\theta$  that corresponded to the graphitic structure of carbon-based materials [59, 60]. In particular, the CA catalyst sample presented the characteristic diffraction peaks of  $\text{CaCO}_3$  according to the PDF-2 database (ICDD: 01-081-2027). These peaks were located at  $\sim 23$ , 29, 31.5, 36, 39, 43, 47, 47.5, and  $48.5$   $2\theta$ . Similar findings have been reported by Galván-Ruiz et al. [61], Buasri et al. [62], and Areerob et al. [63]. It is noteworthy that the CA catalyst sample displayed a more crystalline structure in comparison to the other catalysts where the graphitic structure was not identified in the diffractogram [64]. This result can be attributed to the fact that citric acid is a chelating agent that can form complexes with metals thus

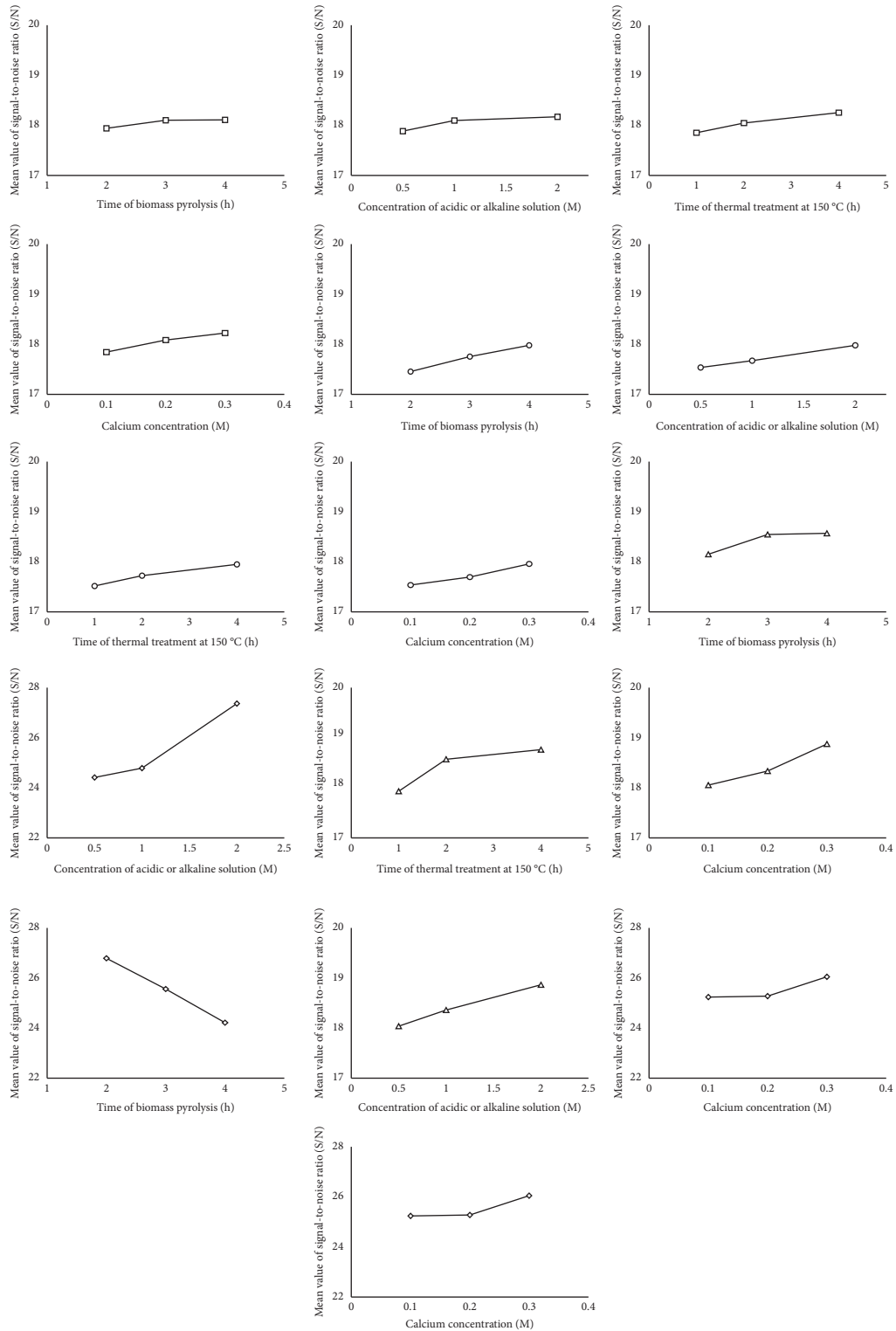


FIGURE 3: The S/N ratio for the preparation conditions of alkaline and acidic heterogeneous catalysts using (□) citric acid (CA), (○) tartaric acid (TA), (△) sulfuric acid (SA), and (◇) potassium hydroxide (K).

favoring their incorporation on the surface of carbon-based supports [65]. The catalyst samples prepared with tartaric acid and potassium hydroxide also showed the presence of  $\text{CaCO}_3$ ; meanwhile, the SA catalyst sample did not show a crystalline structure. Overall, these X-ray diffraction results confirmed the incorporation of calcium moieties into the catalyst samples. These results showed that the presence of calcium functionalities on carbon-based supports generated catalytic properties for oil transesterification, which were consistent with the results reported by other researchers [20, 66–69].

Results of XRF elemental analysis of these samples are reported in Table 2. It was found that the calcium content of CA and K catalyst samples was higher than those obtained for catalysts prepared with SA and TA. As expected, the calcium content in catalysts increased with the calcium concentration used in the functionalization step as shown in the results of 1K, 2K, and 3K samples, see Table 2. Note that the best catalyst showed the highest content of potassium where the highest value was  $\sim 2\%$ . Traces of other elements (e.g., Mg, Si, Cl, Fe, Cu, Zn, Sr, Ti, Cr, Mn, and Ni) were also found in the catalyst samples. It was also observed that the organic content (i.e.,  $\text{CH}_2$ ) decreased with the alkaline concentration used in the catalyst preparation. This result suggested that the organic structure of catalysts was degraded with alkaline treatment. However, the organic content of the CA catalyst was the lowest thus explaining its higher crystallinity than the other catalyst samples. In general, the properties of CA catalyst samples were mainly attributed to the incorporation of calcium species into the material surface, while the catalytic performance of K samples prepared with potassium hydroxide could be related to both potassium and calcium moieties [55–58, 70].

Figure 5 shows the FTIR results for the selected catalyst samples. Spectra of K catalyst samples contained a strong absorption band in the region of  $3500\text{--}3000\text{ cm}^{-1}$  that corresponded to the OH group, and it could be attributed to the alcohols and phenols present in their structure [71]. The absorption band corresponding to the stretching vibration of aliphatic groups was identified between  $2933$  and  $2855\text{ cm}^{-1}$ . Also, the absorption band located at  $\sim 1603\text{ cm}^{-1}$  corresponded to the C=O group, and this band decreased with the increment of KOH concentration utilized to prepare the catalyst. On the other hand, the band of vibrations of aromatic compounds located at  $1446\text{ cm}^{-1}$  also changed with KOH concentration. The absorption band identified at  $892\text{ cm}^{-1}$  was attributed to ring structures. These functional groups were mainly related to the lignocellulosic nature of the precursor utilized to prepare the catalyst [72].

For the case of TA, SA, and CA catalyst samples, the absorption band corresponding to the hydroxyl stretching group was located between  $3500$  and  $3000\text{ cm}^{-1}$ . The absorption band related to the aliphatic group appeared at  $2950\text{--}2800\text{ cm}^{-1}$ , and it decreased depending on the acid used in the catalyst preparation. For instance, the absorption band of the SA sample spectrum was smaller than those of CA and TA samples. This behavior could be attributed to the fact that the acidic treatment modified the surface properties

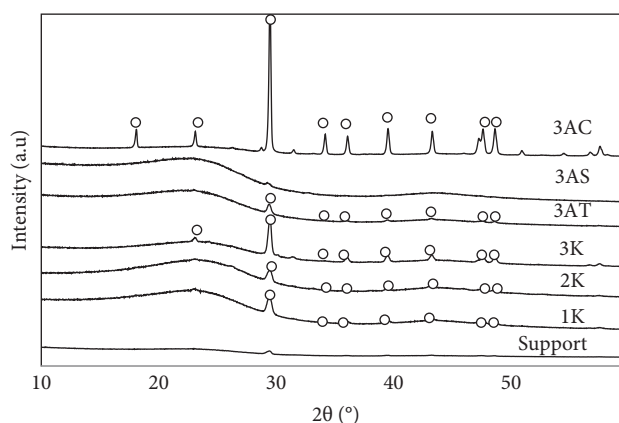


FIGURE 4: X-ray diffraction patterns of alkaline and acidic heterogeneous catalysts used in the transesterification of vegetable oil with methanol to obtain biodiesel.

TABLE 2: Elemental composition obtained from the XRF analysis of alkaline and acidic catalyst samples.

Elements	Catalyst samples					
	1K	2K	3K	3TA	3SA	3CA
$\text{CH}_2$	90.95	89.02	85.58	92.47	91.09	76.35
Ca	7.38	7.83	12.41	7.25	4.79	23.29
K	0.50	2.01	1.19	0.17	0.13	—
S	0.09	0.09	0.06	0.11	2.38	0.03

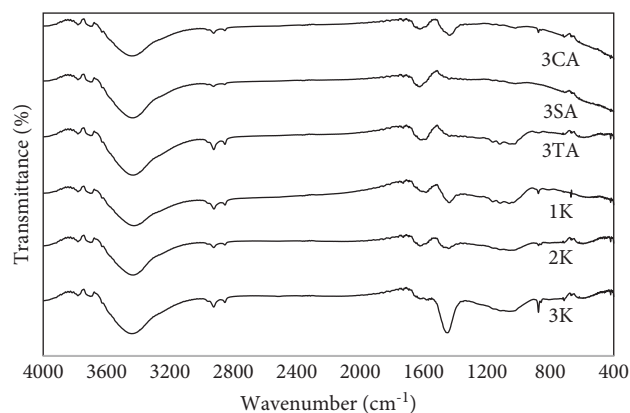


FIGURE 5: FTIR spectra of alkaline and acidic heterogeneous catalysts used in the transesterification of safflower oil with methanol to obtain biodiesel.

by reducing the amount of low molecular weight compounds contained in the lignin structure of biomass precursors [73]. The absorption band identified at  $\sim 1612\text{ cm}^{-1}$  was associated with the carboxylic group, and it could decrease in catalyst samples due to the degradation of the compounds of lignocellulosic precursors.

The specific surface area of the acidic and alkaline heterogeneous catalysts ranged from  $3.8$  to  $129.4\text{ m}^2/\text{g}$  where the best catalyst (i.e., sample No. 3 prepared with potassium hydroxide) showed the highest value. The high activity of this alkaline catalyst could be attributed to this textural property because the active phase was better dispersed on the

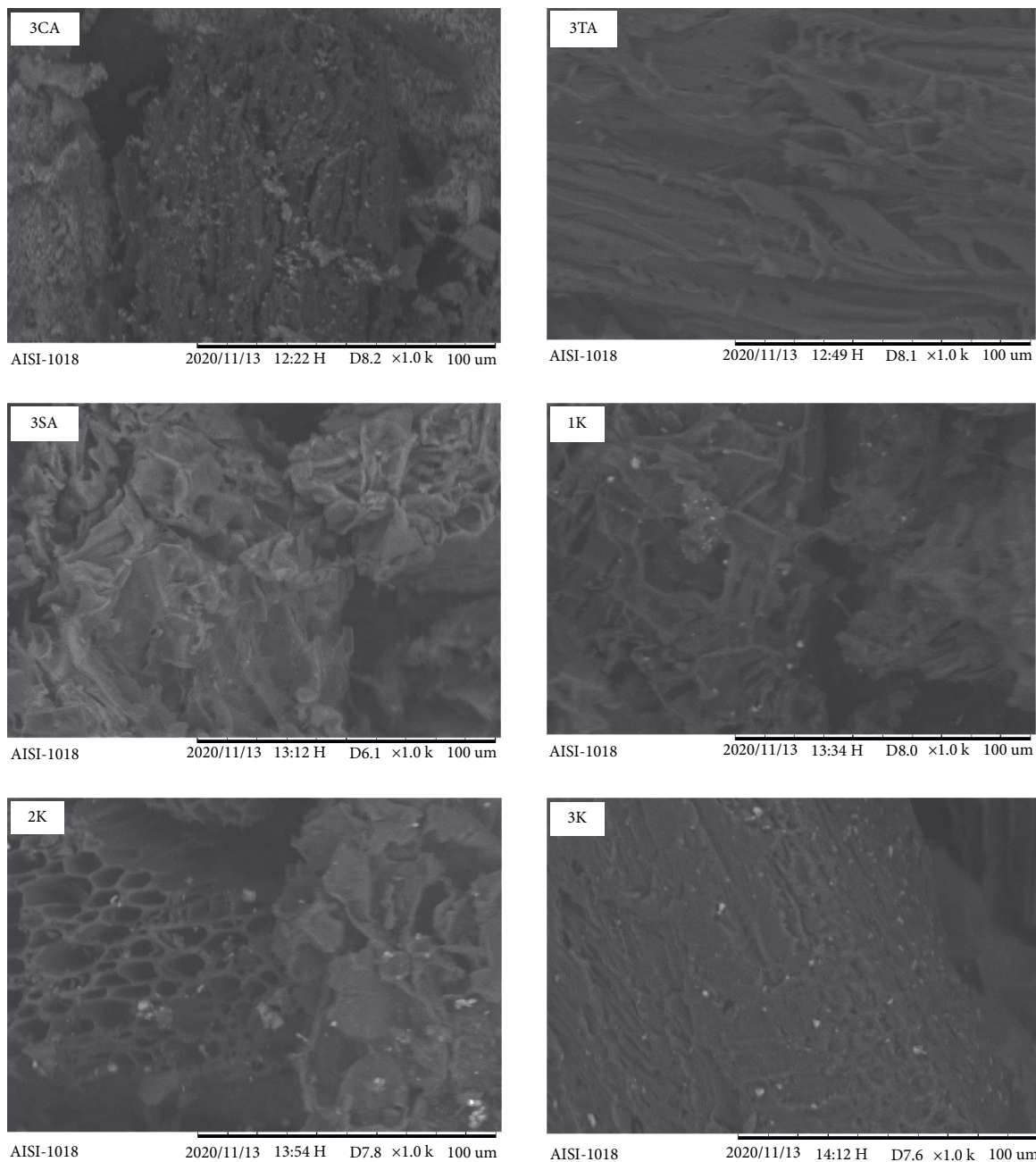


FIGURE 6: SEM images of alkaline and acidic heterogeneous catalysts used in the transesterification of safflower oil with methanol to obtain biodiesel.

available surface functionalities of the carbon-based support [74]. SEM images showed that these catalysts had irregular and compact structures and pores with different magnitudes and shapes, see Figure 6. Catalysts prepared with KOH displayed more diverse morphological changes in their structures. Overall, the results of all analytical techniques confirmed that the catalyst samples showed a different degree of dispersion and anchoring of calcium.

*3.2. Kinetics and Thermodynamics of Vegetable Oil Transesterification to Obtain Biodiesel with the Best Alkaline Catalyst and Its Regeneration.* Transesterification kinetics to

produce biodiesel with the best alkaline catalyst are reported in Figure 7. These kinetic studies showed that the highest percentage of FAME formation occurred during the first 300 min of reaction with the 3K catalyst sample, and the equilibrium reached >360 min. Transesterification kinetics using the 3CA, 3TA, and 3SA catalysts are also reported and compared in Figure 7. For these catalysts, the highest amount of FAME was obtained during the first 240 min, and the equilibrium was achieved at >300 min. The increment of the reaction temperature enhanced the FAME formation of all catalysts. Specifically, the 3K catalyst produced the highest FAME formation up to 97% at 80°C. Note that the molecules were more active at the reaction temperature thus



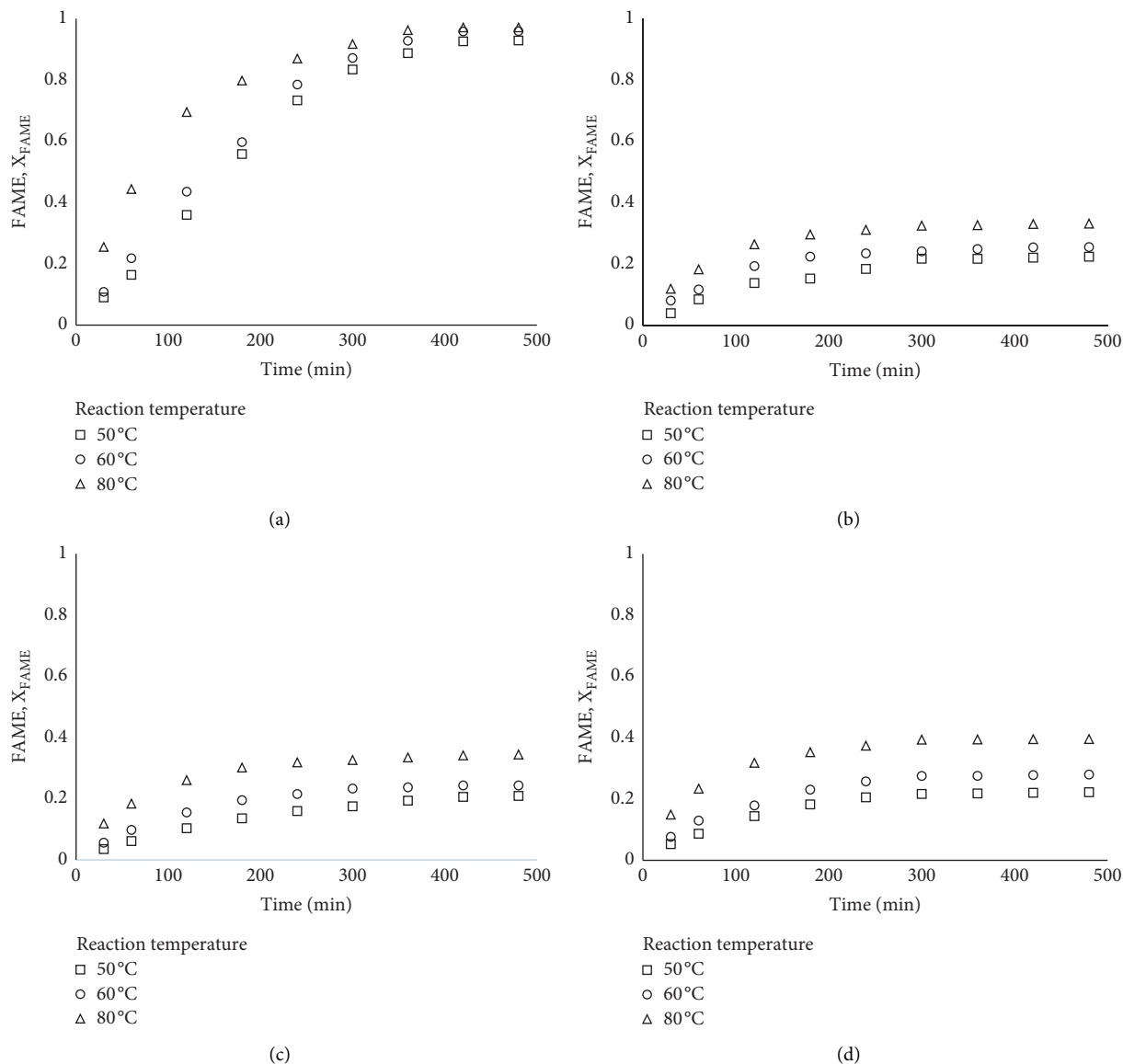


FIGURE 7: Kinetics of transesterification of safflower oil with methanol using the best alkaline and acidic heterogeneous catalysts. Samples: (a) 3K, (b) 3CA, (c) 3TA, and (d) 3SA.

increasing the probability of collision between methanol and vegetable oil molecules, and the reaction accelerated easily and quickly at high temperature [75]. The modeling results of transesterification with the pseudo-first order and pseudo-second order models are given in Table 3.

Both kinetic models provided satisfactory correlations with determination coefficients higher than 0.97. Transesterification rates of the pseudo-first order ranged from 0.002 to 0.010  $\text{min}^{-1}$  for 3K, 0.006 to 0.014  $\text{min}^{-1}$  for 3CA, 0.005 to 0.014  $\text{min}^{-1}$  for 3TA, and 0.007 to 0.015  $\text{min}^{-1}$  for 3SA, respectively. Calculated transesterification rates of the pseudo-second order model were 0.0004–0.007 L/mol-min for 3K, 0.014–0.038 L/mol-min for 3CA, 0.012–0.035 L/mol-min for 3TA, and 0.017–0.036 L/mol-min for 3SA. The pseudo-first order model offered the best data adjustment for all catalysts where its  $R^2 > 0.993$  for 3CA, 3TA, and 3SA catalysts, and

up to 0.979 for 3K catalysts. Estimated transesterification rates increased at the reaction temperature. According to Alenezi et al. [76], the pseudo-first order model assumed that the activity of triglycerides, diglycerides, and monoglycerides were the same and alcohol (i.e., methanol) was in excess.

Table 4 reports the corresponding calculated activation energies for tested catalysts, which ranged from 23.2 to 55.6 kJ/mol. The highest and lowest activation energies were obtained for 3K and 3CA catalysts, respectively. These values suggested that this catalyzed reactive system was chemically reactive rather than mass transfer controlled [77]. Yacob et al. [77] have indicated that the transesterification with heterogeneous catalysts involved activation energies between 26 and 82 kJ/mol, which was consistent with the calculations performed for flamboyant pods-based catalysts.

TABLE 3: Results of the kinetic modeling of transesterification of safflower oil with methanol using the best alkaline and acidic heterogeneous catalysts.

Catalysts	Parameters	Pseudo-first order <sup>1</sup>			Pseudo-second order <sup>2</sup>		
		50°C	60°C	80°C	50°C	60°C	80°C
3K	$k_i$	0.002	0.003	0.010	0.0004	0.001	0.007
	$R^2$	0.979	0.988	0.999	0.978	0.984	0.995
3CA	$k_i$	0.006	0.012	0.014	0.014	0.036	0.038
	$R^2$	0.993	0.997	0.998	0.989	0.990	0.994
3TA	$k_i$	0.005	0.008	0.014	0.012	0.021	0.035
	$R^2$	0.998	0.999	0.996	0.999	0.995	0.991
3SA	$k_i$	0.007	0.010	0.015	0.017	0.026	0.036
	$R^2$	0.999	0.995	0.996	0.992	0.993	0.995

<sup>1</sup> $k_i$ :  $\text{min}^{-1}$ ; <sup>2</sup> $k_2$ : L/mol·min.

TABLE 4: Calculated activation energies of transesterification of safflower oil with methanol using the best alkaline and acidic heterogeneous catalysts.

Catalysts	Ea, kJ/mol
3K	55.6
3CA	23.2
3TA	30.3
3SA	25.3

The results of the catalyst regeneration are shown in Table 5. For all catalysts, the FAME formation percentage decreased after each regeneration cycle where it ranged from 95 to 11.8%. For example, the 3K catalyst showed 95% of FAME formation in the first cycle, 91.8% in the second cycle, and 75.9 and 62.2% in the third and fourth cycles, respectively. Overall, 3CA, 3TA, and 3SA catalysts showed a more drastic reduction of their properties after regeneration in comparison to the best 3K catalyst. Even after four regeneration cycles, the alkaline catalyst outperformed the acidic catalysts, see results in Table 5. This result can be attributed to the leaching of active sites (e.g., K and Ca moieties) in the reaction media [78]. This leaching could be due to break of active sites and alcohol bonds and the formation of  $\text{K}^+$ ,  $\text{Ca}^+$ , and  $\text{CH}_3\text{O}^-$  during oil transesterification [34]. In addition, the loss of catalyst activity was attributed to the adsorption of oil, FFA, glycerol, and methyl esters on the surface of catalysts, which caused their deactivation [32, 33, 79]. These results agreed with the study performed by Catarino et al. [31] thus concluding that the catalyst regeneration is viable for a potential industrial application.

According to the literature, the percentage of FAME formation can range from 65 to 100% using acidic and alkaline heterogeneous catalysts. In particular, Chen et al. [80] reported the use of carbonized Ti-SBA15 that was synthesized at 400–500°C as an acidic catalyst in the transesterification of jatropha oil where 81.7% of FAME formation was obtained. Zhang et al. [81] prepared a carbon-based solid acid microspheric material obtained via hydrothermal precipitation and pyrolysis of glucose, which was used as an acidic catalyst. This material showed a FAME formation of 94% under tested operating conditions. Devi

TABLE 5: Results of the reactivation of the best alkaline and acidic heterogeneous catalysts used in transesterification of safflower oil with methanol.

Catalysts	FAME (%) for the regeneration-reaction cycle			
	1st	2nd	3rd	4th
3CA	25.0	23.0	16.7	13.7
3TA	24.1	22.1	15.5	11.8
3SA	28.0	26.2	18.7	13.6
3K	95.0	91.8	75.9	62.2

et al. [43] reported the evaluation of  $\text{SO}_3\text{Na}$ -carbon as an acidic catalyst in biodiesel production using sunflower oil with 99% of FAME formation. Dhawane et al. [82] analyzed the synthesis and application of an alkaline carbon-based catalyst obtained from flamboyant pods and their modification with KOH. This catalyst was tested with rubber seed oil obtaining 89.8% FAME formations. Zhao et al. [44] tested the use of  $\text{K}_2\text{CO}_3$ -pomelo peel biochar modified with KOH as a catalyst in the transesterification of palm oil where a FAME formation of 82% was achieved. As indicated, the best alkaline catalyst reported in this manuscript showed a FAME formation up to 95%. Therefore, the preparation and functionalization protocol to obtain this catalyst contributed to enhancing its properties for biodiesel production. It also showed the synergic effect of calcium and potassium to enhance the catalytic properties of carbon-based materials for obtaining biodiesel. Finally, the industrial production of biofuels employing heterogeneous catalysts can offer additional advantages than those obtained with homogeneous catalysts [11].

#### 4. Conclusions

The functionalization and activation of carbon-based chars with calcium, acidic, and alkaline solutions are of paramount importance to prepare heterogeneous catalysts with tailored properties for the production of FAME via vegetable oil transesterification. Results showed that the alkaline and calcium-based functionalization and activation of chars obtained from flamboyant pods were the best procedure to prepare an effective heterogeneous catalyst for biodiesel production via oil transesterification. The heterogeneous catalysts prepared with potassium hydroxide outperformed, up to three times, the FAME formation of those catalysts obtained with citric, sulfuric, and tartaric acids. These alkaline heterogeneous catalysts achieved FAME formations of >95% in the transesterification of safflower oil with methanol at 50–80°C. The performance and properties of these alkaline catalysts were associated with the presence of a higher specific surface area and contents of calcium and potassium moieties than those of the acidic heterogeneous catalysts. These alkaline catalysts also showed a better performance than acidic catalysts after four regeneration-reaction cycles. In summary, the alkaline heterogeneous catalyst obtained from KOH and calcium-based functionalization and activation of flamboyant pod chars could be an interesting alternative to intensify the production of biofuels

and other added-value products obtained from vegetable oil transesterification.

## Data Availability

The data are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

## Authors' Contributions

L.L. Díaz-Muñoz was responsible for conceptualization, methodology, investigation, formal analysis, and writing the original draft. H.E. Reynel-Avila was responsible for conceptualization, supervision, project administration, and writing, reviewing, and editing the manuscript. D.I. Mendoza-Castillo was responsible for investigation and writing, reviewing, and editing the manuscript. A. Bonilla-Petriciolet was responsible for funding acquisition, supervision, and writing, reviewing, and editing the manuscript. J. Jáuregui-Rincón was responsible for investigation and writing, reviewing, and editing the manuscript.

## Supplementary Materials

Supplementary materials contain the description of characterization techniques and the calculations and results of ANOVA. (*Supplementary Materials*)

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