



The Effect of Mole Ratio Natural-CaCO₃/KF in the Synthesis of KCaF₃ Perovskite Base Catalyst

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<https://doi.org/10.14710/jksa.27.8.388-394>

Article Info

Article history:

Received: 02nd November 2023

Revised: 24th August 2024

Accepted: 26th August 2024

Online: 31st August 2024

Keywords:

Perovskite Catalyst; KCaF₃;
 natural-CaCO₃; KF

Abstract

The KCaF₃ perovskite catalyst was successfully synthesized by reacting limestone (natural-CaCO₃) with potassium fluoride (KF). The synthesis of the KCaF₃ catalyst was conducted with several variations in the mole ratio of CaCO₃ to KF (1:1, 1:2, and 1:3). The research results showed that the addition of KF can affect the characteristics of the catalyst. The optimal catalyst is the KCaF₃ catalyst with a mole ratio variation of 1:3. X-ray diffractometer analysis revealed that the highest KCaF₃ phase composition reached 74.05%, while thermogravimetric analysis indicated a CaCO₃ concentration of 34.50%. Surface Area Analyzer analysis shows that KCaF₃ has the largest surface area, which is 187.1 m²/g. This catalyst efficiently facilitated the transesterification of palm oil, yielding 93.4% biodiesel.

1. Introduction

Calcium-based catalysts for transesterification can be synthesized from various materials, including KF/CaO [1, 2, 3, 4, 5, 6, 7, 8]. The reaction between KF and CaO results in the formation of the perovskite KCaF₃, which is a basic catalyst known for its high reactivity in transesterification processes. However, Ye *et al.* [6] found that KCaF₃, whether used alone or as a component in KF/CaO, exhibited no catalytic activity in biodiesel synthesis. Instead, its primary function is to enhance the mechanical strength and structural stability of the catalyst, thereby boosting the catalytic performance of KF/CaO in the transesterification reaction. Additionally, KCaF₃ can also form from the reaction of KF with Ca(OH)₂. In nature, CaO and Ca(OH)₂ are derived from CaCO₃.

Nurcahyo *et al.* [9] successfully synthesized the KCaF₃ catalyst using Ca(OH)₂ containing CaCO₃ impurities. Their findings revealed that KF was reactive not only with Ca(OH)₂ but also with CaCO₃. This demonstrates that natural CaCO₃ can serve as a precursor for KCaF₃ formation, enabling the production of an economically viable catalyst in terms of both cost and synthesis route. Enhancing the activity of calcium species can be achieved by reacting natural CaCO₃ with added KF salt to form KCaF₃ perovskite. The addition of KF increases the catalyst's activity by creating new, more

reactive active sites until an optimal point is reached [3]. The novelty of this research lies in the utilization of natural CaCO₃ as a precursor for synthesizing KCaF₃. By employing natural CaCO₃, the synthesis pathway for KCaF₃ from natural materials can be shortened, leading to the development of a more economical catalyst.

Building on the provided background, this research aims to produce heterogeneous base catalysts for biodiesel production using limestone (natural CaCO₃) as the raw material. The study explores variations in the mole ratio of CaCO₃ to KF (potassium fluoride) at 1:1, 1:2, and 1:3. The starting material was characterized using X-ray fluorescence (XRF), thermogravimetric analysis (TGA), and X-ray diffraction (XRD). The resulting catalyst was characterized using TGA, XRD, Fourier-transform infrared spectroscopy (FTIR), and surface area analysis (SAA).

2. Experimental

2.1. Tools and Materials

The equipment used in this research included a porcelain mortar, spatula, glass stirrer, dropper pipette, beaker glass, watch glass, 100 mesh sieve, 200 mesh sieve, crucible, crucible clamp, oven, and furnace. Advanced instruments utilized were a Bruker D8 Advance X-ray diffractometer (XRD), Bruker S2 Ranger X-ray

fluorescence (XRF) spectrometer, TG-DTA 7300 thermogravimetric analyzer (TGA), Shimadzu IR Prestige-21 FTIR spectrometer, Quantachrome Nova e-series surface area analyzer (SAA), and Rietica Software for data analysis.

The materials used in this research were limestone (natural-CaCO₃) sourced from Jimbung Village in Klaten, potassium fluoride (KF.2H₂O, Xylong Scientific, AR grade), mineral-free water, methanol (Merck), and palm oil (Filma).

2.2. Preparation and Characterization of KCaF₃ Catalyst

Limestone was initially crushed and ground into a finer texture using a porcelain mortar and pestle. The ground limestone was then sieved through a 200-mesh sieve until a 100–200 g sample was obtained. A 5 g sample was heated at 900°C for 3 hours in a furnace, after which its elemental content was analyzed using XRF. The remaining limestone sample was heated to 110°C for 3 hours in an oven and subsequently analyzed using XRD and TGA to determine the CaCO₃ content.

The KCaF₃ catalyst was synthesized with varying CaCO₃ mole ratios, as detailed in Table 1. Specified amounts of CaCO₃ (200 mesh) and KF were mixed and ground using a porcelain mortar for 15 minutes, allowing the mixture to coagulate due to the absorption of water vapor from the environment. Subsequently, approximately 4 mL of water was added to the mixture, followed by an additional 15 minutes of grinding. The resulting dough was then dried at 120°C for 6 hours.

The CaCO₃ and KF mixture was then crushed and sieved through a 100-mesh sieve. A 7 g mixture was placed in a quartz crucible and calcined for 10 minutes in a Rapid Thermal Annealing (RTA) furnace at 500°C, with a heating rate of 20°C per minute. The RTA furnace, which used an infrared lamp as the heating element, allowed for high heating rates. The resulting material was further crushed and sieved using a 100-mesh sieve. The powder was characterized using XRD, FTIR, SAA, and TGA instruments, with XRD characterization extensively refined using Rietica software. The synthesized catalyst was then tested for its activity in the transesterification of palm oil. The transesterification was conducted at 65°C, with an oil-to-methanol ratio of 1:12, a catalyst loading of 5% by palm oil weight, and a reaction time of 25 minutes. The mass fraction of biodiesel in the palm oil was determined using FTIR with non-linear standards. The FTIR data used was the absorbance at a wavenumber of 1200 cm⁻¹, corresponding to the O-CH₃ stretching vibration.

Table 1. The CaCO₃: KF mole ratio with 10 g of CaCO₃

CaCO ₃ :KF mole ratio	Calcination temperature (°C)
1:1	500
1:2	500
1:3	500

3. Results and Discussion

3.1. Characteristics of the Synthesized KCaF₃ Catalyst

3.1.1. Elemental Composition of the Natural-CaCO₃

The results of the XRF analysis, which aimed to identify the components present in calcined natural limestone (natural-CaCO₃), are summarized in Table 2. The analysis reveals a significantly high CaO content in the limestone, approximately 96.96%. Other components are present in much smaller quantities, including SiO₂, Fe₂O₃, Al₂O₃, P₂O₅, K₂O, Cl, SO₃, SrO, MnO, and SnO₂, each comprising less than 1% of the total composition.

3.1.2. Crystallinity Analysis of CaCO₃ and KCaF₃

The identification of the limestone phase (natural-CaCO₃) and the KCaF₃ catalyst with varying mole ratios is shown in Figures 1 and 2. The diffractogram of limestone (natural-CaCO₃), when compared to the ICSD #18164 CaCO₃ standard, exhibits a similarity, as depicted in Figure 1. Notably, the diffractogram indicates high crystallinity in limestone (natural-CaCO₃), evident from sharp and small peaks.

In Figure 2, the diffractogram of the KCaF₃ catalyst reveals several observed phases, including KCaF₃, CaCO₃, and Ca(OH)₂. The formation of the KCaF₃ phase occurs during the KF-CaCO₃ impregnation stage, where the process can generate heat up to 120°C [3]. The KCaF₃ phase is identified in two crystal forms: monoclinic and orthorhombic, while the cubic KCaF₃ form is not identified due to its very low intensity. According to Nurcahyo *et al.* [9], monoclinic KCaF₃ crystals are observed at 2θ values of 20.08°, 28.6°, 40.93°, 51.01°, and 59.54°, whereas orthorhombic KCaF₃ crystals appear at 2θ values of 35.54°, 37.17°, 48.10°, and 68.23°. Research by Wen *et al.* [3] indicates that the formation of the KCaF₃ phase in the material enhances catalytic activity and stability due to its strong affinity for the methoxy group, thereby increasing the rate of the transesterification reaction.

Table 2. Component of limestone (natural-CaCO₃)

Component	Concentration (%)
CaO	96.96
SiO ₂	0.93
Fe ₂ O ₃	0.59
Al ₂ O ₃	0.47
P ₂ O ₅	0.29
K ₂ O	0.27
Cl	0.20
SO ₃	0.14
SrO	0.08
MnO	0.02
SnO ₂	0.01

Table 3. Peak diffractogram analysis of the KCaF₃ catalyst

Compound	Peak 2θ (°)			
	Reference	KCaF ₃ 1:1	KCaF ₃ 1:2	KCaF ₃ 1:3
CaCO ₃ [10]	23.00	-	22.83	22.56
	29.00	29.30	29.57	29.55
	33.15	-	32.24	32.49
	45.86	45.67	45.69	-
Ca(OH) ₂ [10]	34.00	-	33.88	33.87
	47.20	47.94	47.40	47.35
	50.82	-	50.87	50.84
	54.50	54.56	54.50	-
	63.00	62.96	62.98	-
KCaF ₃ Monoclinic [9]	20.08	20.01	19.82	20.16
	28.60	28.31	28.29	28.69
	40.93	40.71	41.14	41.09
	51.01	-	51.14	51.08
	59.54	58.88	59.60	59.57
KCaF ₃ Orthorhombic [9]	35.54	35.04	35.02	35.50
	37.17	-	-	38.40
	48.10	48.39	-	48.53
	68.23	-	67.56	67.50

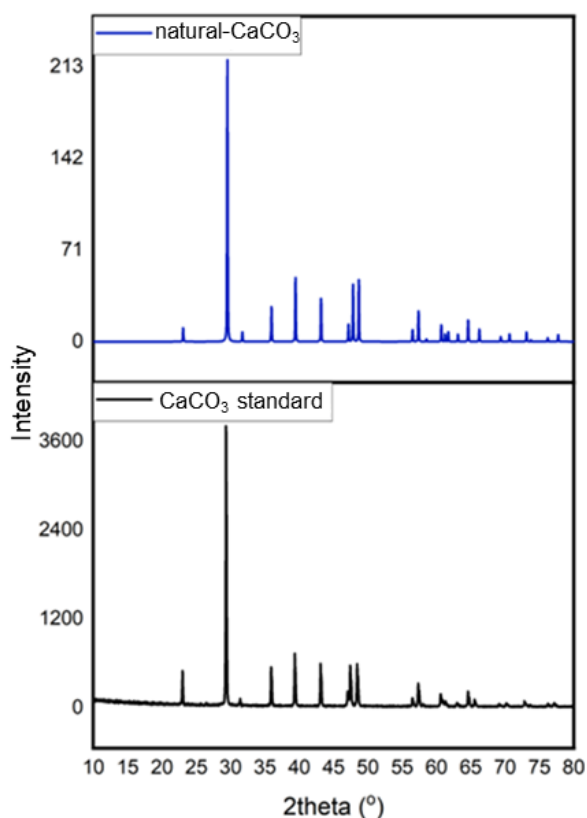


Figure 1. Diffractogram of limestone (natural-CaCO₃) and CaCO₃ standard (ICSD #18164)

In addition to the KCaF₃ phase, the diffractogram also shows the presence of other compounds, such as CaCO₃ and Ca(OH)₂. The detection of the CaCO₃ phase at low intensity suggests the presence of unreacted residual CaCO₃ material. In the study by Wen *et al.* [3], no Ca(OH)₂ peak was detected when the calcination temperature reached 600°C. In contrast, a Ca(OH)₂ peak was observed in the present study, albeit with relatively low intensity. This discrepancy is likely due to the difference in the catalyst calcination process, particularly the lower temperature of 500°C used in the current study. The presence of Ca(OH)₂ in the catalyst could potentially interfere with the catalytic process, as it may lead to the formation of soap through saponification.

Further analysis for phase composition determination was performed using refinement analysis via the Le Bail method with Rietica software. The reliability values (R) obtained from the refinement results, including R_p, R_{wp}, and χ² (GoF), serve as indicators of data acceptability. Lower reliability values indicate better acceptability of the analyzed phase or standard. Specifically, for the χ² (GoF) parameter, the reliability value has an acceptability threshold, with a maximum value of 4 [10, 11, 12].

Table 4. Phase composition and Rp, Rwp, χ^2 (GoF) values of samples with all standards

Standard	ICSD code	Mole fraction (%)			
		CaCO ₃ -nature	KCaF ₃ 1:1	KCaF ₃ 1:2	KCaF ₃ 1:3
CaCO ₃	#18164	100	19.58	4.10	3.92
Monoclinic KCaF ₃	#85320	-	48.97	58.37	58.74
Orthorhombic KCaF ₃	#153628	-	12.09	14.42	14.35
Cubic KCaF ₃	#154073	-	0.81	0.96	0.96
KO ₂	#87183	-	8.83	10.53	10.48
K ₂ O	#44674	-	9.73	11.61	11.55
Rp		11.49	16.17	17.29	16.90
Rwp		15.97	23.95	23.52	23.31
χ^2 (GoF)		1.406	2.925	2.736	2.642

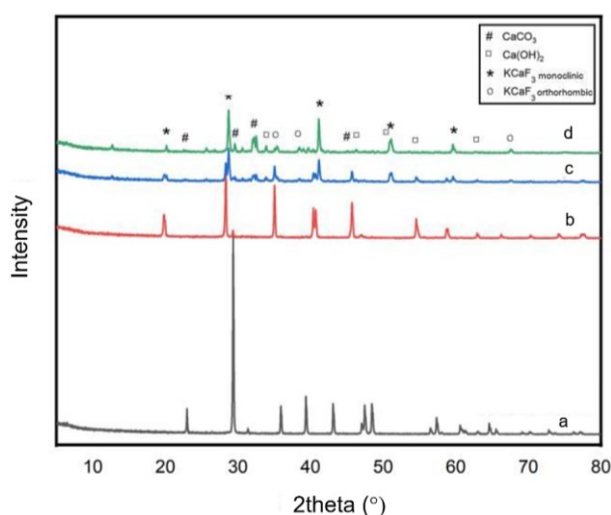


Figure 2. The diffractogram of limestone and KCaF₃ catalyst with varying mole ratios a) limestone, b) material with molar ratio CaCO₃: KF 1:1, c) material with molar ratio CaCO₃: KF 1:2, d) material with molar ratio CaCO₃: KF 1:3

The predominant crystal form of KCaF₃ is found to be monoclinic, followed by orthorhombic and cubic, as indicated by the phase composition percentages presented in Table 4. Additionally, the reliability values (R) with residual factor parameters (Rp and Rwp) for the KCaF₃ catalyst exhibit a relatively high value compared to the residual factor of natural-CaCO₃. This discrepancy is likely due to undetected peaks in the analysis. Nevertheless, the reliability value (R) for the χ^2 (GoF) parameter on the KCaF₃ catalyst remains below the acceptable limit of 4, indicating the overall acceptability of the data.

Based on the refinement results of the three catalysts, it can be deduced that the KCaF₃ catalyst with a mole ratio of 1:3 exhibits the highest KCaF₃ phase composition compared to the other two variations, specifically 74.05%. This observation indicates that the addition of KF has a significant impact on increasing the KCaF₃ phase composition. Consequently, the KCaF₃ catalyst with a mole ratio of 1:3 is the optimal catalyst based on XRD analysis.

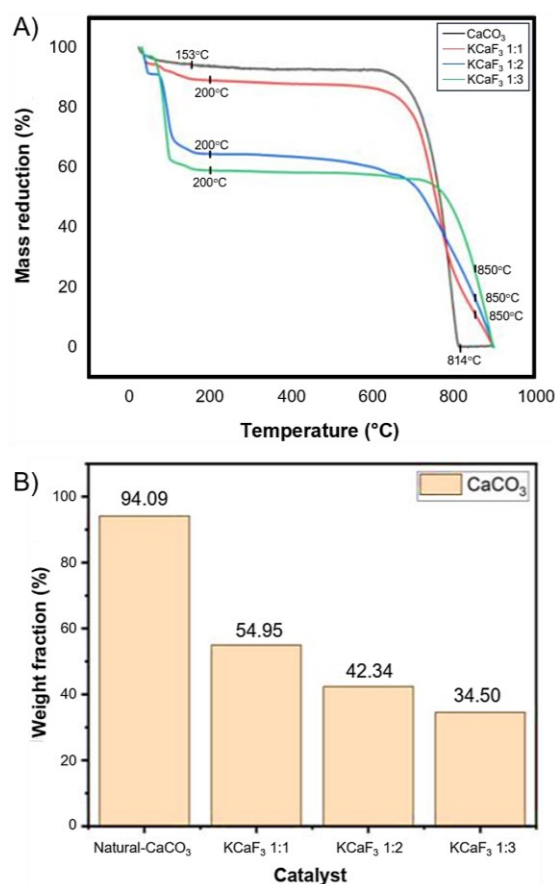


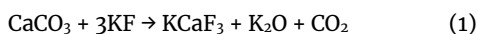
Figure 3. A) TGA analysis of limestone and KCaF₃ catalyst with variations in moles of 1:1, 1:2, 1:3, and B) reduction of CaCO₃ in KCaF₃ catalyst based on TGA analysis

3.1.3. Thermal Analysis

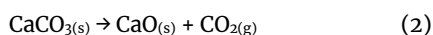
Thermal analysis using Thermogravimetry Analysis (TGA) was conducted in an air atmosphere with a temperature increase rate of 10°C/minute and a temperature range ranging from room to 900°C. As depicted in Figure 3A, a decrease in mass is observed in the temperature range of 153-200°C, indicating the loss of water compounds present in both the starting material and the catalyst. Correia *et al.* [13] reported that the mass decrease in the temperature range of 50-400°C suggested

the physical adsorption of water onto the material's surface. The variation in the percentage decrease in mass during water absorption in the KCaF_3 catalyst material is attributed to the hygroscopic nature of KF . Consequently, an increased amount of added KF intensifies its water-attracting capacity. Furthermore, the reduction in mass in the temperature range of $814\text{--}850^\circ\text{C}$ signifies the loss of CO_2 compounds, a result of the decomposition of CaCO_3 into CO_2 and CaO .

Thermal analysis using TGA aims to determine the concentration of limestone and the KCaF_3 catalyst, as depicted in Figure 3B. Limestone exhibits a mass CaCO_3 concentration of 94.09%, while the 1:3 KCaF_3 catalyst displays the lowest CaCO_3 concentration at 34.50%. This outcome suggests that the 1:3 KCaF_3 catalyst, having the highest ratio of KF , facilitates the conversion of a greater amount of CaCO_3 into KCaF_3 . Examining the reaction between CaCO_3 and KF in Equation (1), it becomes apparent that the KCaF_3 catalyst with a mole ratio of 1:3 is the optimal catalyst, evidenced by the substantial reactant coefficient in the reaction.



The three variations in the mole ratio of the KCaF_3 catalyst yield KCaF_3 products. However, the reaction is incomplete for catalysts with mole ratios of 1:1 and 1:2, indicating that not all reactants are converted into KCaF_3 products. Additionally, referring to the CaCO_3 decomposition reaction equation (Equation (2)), the percentage of mass reduction reflects the quantity of CO_2 gas formed. Consequently, the moles of CO_2 obtained are equivalent to the moles of CaCO_3 , allowing the determination of the mass percent of CaCO_3 .



As shown in Figure 3B, increasing the amount of KF added to the catalyst results in a reduced concentration of CaCO_3 . This observation supports the understanding that higher KF amounts enhance the conversion of CaCO_3 into the KCaF_3 compound. This trend is consistent with the XRD crystallinity analysis results, which show an increased composition of the KCaF_3 phase and a decreased concentration of CaCO_3 , indicating successful conversion into KCaF_3 .

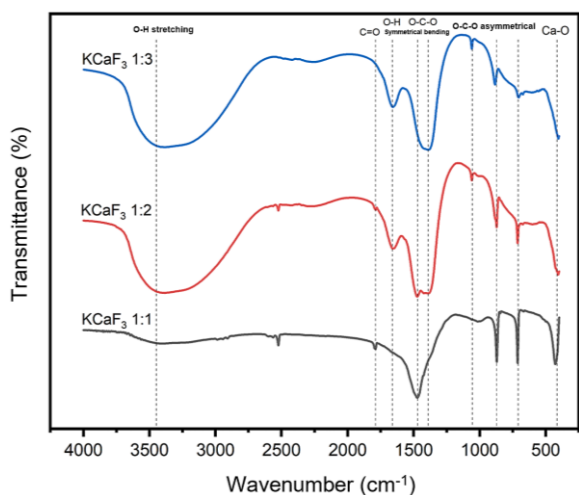


Figure 4. FTIR spectra of 1:1, 1:2, and 1:3 KCaF_3 catalysts

3.1.4. Functional Group Analysis

Qualitative analysis of the functional groups in the KCaF_3 catalyst was performed by comparing the absorption patterns across three different mole ratios, as shown in Figure 4 and Table 5. The absorption in the $3382\text{--}3405\text{ cm}^{-1}$ range corresponds to the typical OH stretching vibration of hydroxy groups within the KCaF_3 compound, interacting with water molecules present in the catalyst material. The variation in peak magnitude for the hydroxy absorption in Figure 4 indicates that increasing the amount of added KF results in higher hydroxy absorption. This is due to the hygroscopic nature of the KF compound, which leads to an increased production of hydroxy groups. Additionally, the wavenumbers between $1658\text{--}1659\text{ cm}^{-1}$ correspond to OH bending vibrations from water molecules in the particle area, bound to interlayer anions.

Absorptions at wavenumbers 1465, 1389, 873, and 713 cm^{-1} are characteristic of CaCO_3 [9]. The 1:1 KCaF_3 catalyst exhibits CaCO_3 absorptions at 1473, 871, and 713 cm^{-1} , with sharper peaks compared to the 1:2 and 1:3 KCaF_3 catalysts. This distinction is attributed to the influence of the added KF compound on the formation of the KCaF_3 catalyst. The symmetric stretching vibration of carbonate ions (OCO) from natural- CaCO_3 is observed at 1473 cm^{-1} . Simultaneously, asymmetric stretching vibrations of OCO are evident in the $1014\text{--}1060\text{ cm}^{-1}$ range. The $\text{C}=\text{O}$ stretching of carbonate ions from CaCO_3 is identified at wavenumbers between 1658 and 1794 cm^{-1} .

3.1.5. Analysis of Specific Surface Area and Pore Diameter

The specific surface area characteristics were analyzed to assess the effect on catalyst activity, particularly related to the adsorption phenomenon. A larger specific surface area indicates a higher capacity for substance adsorption. Comprehensive data on the specific surface area and pore diameter of the catalyst are provided in Table 6.

Table 5. Tabulation of KCaF_3 functional groups for various variations in mole ratios

Functional group	Wavenumber (cm^{-1})			
	Reference	KCaF_3 1:1	KCaF_3 1:2	KCaF_3 1:3
OH stretching	3460 [11]	3382.32	3405.47	3384.25
	1621 [11]			
OH bending	1647 [12]		1659.82	1658.85
	1640 [9]			
OCO symmetry stretching	1475 [12]	1473.68;	1473.68;	884.40;
	875, 712 [14]	871.86;	872.83;	705.01
		713.69	713.89	
OCO asymmetry stretching	1074; 864 [12]	1014.6	1060.89	1060.89
C=O stretching	1500–2000 [11]	1794.84	1788.09	1658.85

Table 6. Effect of KF addition on the surface area and pore diameter of the catalyst

Catalyst	Specific surface area (m ² /g)	Pore diameter (nm)
KCaF ₃ 1:1	11.79	9.036
KCaF ₃ 1:2	25.45	6.620
KCaF ₃ 1:3	187.1	4.380

According to the data in Table 6, the KCaF₃ catalyst with a KF mole ratio of 1:3 exhibits the largest surface area and the smallest pore diameter, specifically 187.1 m²/g and 4.380 nm, respectively. This suggests that adding KF to the initial limestone material increases the surface area, with the effect proportional to the amount of KF added. This finding is supported by a study by Anbia *et al.* [14], which indicates that the addition of potassium halide can enhance the catalyst's surface area.

The decrease in pore diameter with increasing KF addition indicates that the pore size diminishes as more KF is added. Concurrently, the increase in surface area can be attributed to the formation of a new structure, specifically KCaF₃, during the impregnation of the initial material with KF [15]. Sing [16] classified the three catalysts as mesoporous based on pore size, with pore diameters varying with mole ratios of 1:1, 1:2, and 1:3, measuring 9.03, 6.620, and 4.38 nm, respectively.

Research by Marinković *et al.* [17] indicates that the CaCO₃ precursor has a pore diameter of 41 nm. In this study, smaller pore diameters were observed compared to the initial material, which can be attributed to the addition of KF. This addition influenced the increase in surface area and reduction in pore diameter. The increase in surface area with more KF is expected because CO₂ release from the reaction creates additional pores (as described in Equation (2)). More KF leads to more CO₂ release, resulting in the formation of more pores and, thus, an increased surface area. Consequently, a catalyst with a larger surface area is anticipated to exhibit superior characteristics and activity compared to one with a smaller surface area.

3.1.6. Catalyst Activity Test in the Transesterification

The catalytic activity of the three catalysts was compared under identical reaction conditions, with activity assessed based on the mass fraction of biodiesel produced. The results of the catalyst activities are presented in Table 7. Referring to Figure 3 and Table 7, it can be observed that lower CaCO₃ content in the catalyst correlates with higher catalyst activity. Additionally, Tables 6 and 7 show that a higher surface area of the catalyst is associated with increased activity.

Table 7. Mass fraction of biodiesel

Catalyst	Mass fraction of biodiesel (%)
KCaF ₃ 1:1	undetected
KCaF ₃ 1:2	61.5
KCaF ₃ 1:3	93.5

4. Conclusion

The KCaF₃ catalyst was successfully synthesized from limestone (natural-CaCO₃) with the addition of potassium fluoride (KF). In this experiment, the most effective catalyst for catalyzing the transesterification of palm oil was the perovskite KCaF₃ with a 1:3 molar ratio. The goal of shortening the synthesis pathway for KCaF₃ using natural materials was achieved by employing natural-CaCO₃ precursors, eliminating the need for CaO and Ca(OH)₂.

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