



Synthesis and Characterization of Natural $\text{Ca(OH)}_2/\text{KF}$ Superbase Catalyst for Biodiesel Production from Palm Oil

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ABSTRACT

The natural $\text{Ca(OH)}_2/\text{KF}$ superbase catalyst was synthesized by grinding and calcinations with a rapid thermal annealing method. It was applied to transesterification of palm oil into biodiesel. The effect of molar ratio Ca(OH)_2 to KF and calcinations temperature on the catalyst character and the catalytic activity was investigated. The catalysts were characterized by XRD, FTIR, CO_2 -TPD, surface area, and TGA. The results indicated that natural Ca(OH)_2 reacted to KF in forming monoclinic and orthorhombic KCaF_3 . The monoclinic KCaF_3 was produced by reaction between Ca(OH)_2 and KF, whereas the orthorhombic KCaF_3 was produced by reaction between CaCO_3 impurities and KF. The best catalyst was natural $\text{Ca(OH)}_2/\text{KF}$ with molar ratio of Ca(OH)_2 to KF 0.8:1 and calcinations at 500 °C. The catalyst was able to convert 97.6 % oil into biodiesel within 1 min. at 5 % catalyst, molar ratio oil/methanol of 1/12, reaction temperature of 65 °C.

Keyword: Natural $\text{Ca(OH)}_2/\text{KF}$, Superbase, Biodiesel, Palm oil.

INTRODUCTION

Among the studied heterogeneous catalysts, there was alkaline earth basic oxide such

3relative order of effectiveness to catalyze transesterification was $\text{BaO} \sim \text{SrO} > \text{NaOH} \gg \text{CaO} \sim \text{MgO}$. The SrO catalyst was further examined due



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to toxicity concerning with BaO⁴. Calcium-based heterogeneous catalysts were very intriguing to develop. It is due to natural calcium abounds in the CaCO₃ phase. The CaCO₃ can be converted to CaO and Ca(OH)₂. Their catalyst activity can be

enhanced by loading potassium fluoride. The loading will produce superbase catalyst KCaF₃⁵⁻¹¹. Some data concerning a state of transesterification and catalyst preparation for various catalysts of CaO and Ca(OH)₂ loaded KF are shown on Table 1.

Table 1: Literature of transesterification on CaO/KF

Catalyst	CaO to KF or Ca(OH) ₂ to KF (mol/mol)	Calcinations		Catalyst weight (%)	Transesterification			Methylester yield (%)
		T (°C)	t (h)		Oil to Methanol (mol/mol)	T (°C)	t (min.)	
KF/CaO ⁵	4.14/1	600	4	4	12-Jan	65	150	96.8
CaO/KF ¹¹	1/1.036	500	5	2.1	12-Jan	65	20	99.9
ZnO/Ca(OH) ₂ /KF ⁹	1-Jan	400	6	3	12-Jan	65	90	97.6
Na ₂ SiO ₃ /CaO/KF ¹⁰	1/1.5	400	4	3	10-Jan	65	30	97.1

The data in Table 1 indicate that the CaO/KF is a good catalyst for transesterification. Both molar ratio of CaO/KF and calcinations temperature have an effect on this catalyst activity. The best of the molar ratio of CaO/KF is around 1-1.5. On the best molar ratio, transesterification of triglyceride was almost complete. The good calcinations temperature in order to prepare this catalyst is about 400-500 °C. Catalyst of CaO/KF without other oxides has higher activity than the catalyst plus other oxides. The catalysts were calcined using normal heating about 400-600 °C for 4-6 hours. The calcination was just wasteful of energy. In order to save energy, calcination with other methods shall be attempted. One such method is rapid thermal annealing (RTA). This method allows calcination process performed in a short time and rapid heating rate. The RTA method for calcination is superior to the CFA (conventional furnace annealing) method for reducing calcination timing budget and yielding relatively high specific surface areas of tin oxide powders¹². Calcination using the RTA method produced a smaller crystalline size of the oxide than those produced using the CFA method at the same temperature¹².

In this study, Ca(OH)₂ was obtained from natural CaCO₃ in Indonesia. The authors chose Ca(OH)₂ and did not opt for CaO as its precursor. This selection is based on consideration that CaO/KF is prepared by adding water. If CaO was added by water, it will produce Ca(OH)₂. The

possibility of using Ca(OH)₂ was more effective than CaO in formation of KCaF₃. The Ca(OH)₂/KF catalyst was prepared by simple grinding, thus it was calcined with rapid thermal annealing method. The catalyst was characterized by X-ray diffraction (XRD), FTIR, CO₂-TPD, TGA, and Surface Area Analyzer. It is applied to transesterification of palm oil and the resulting biodiesel was detected by H-NMR.

MATERIALS AND METHODS

Natural Ca(OH)₂ was obtained from home industry in Klaten, Indonesia. Reagent grade potassium fluoride and methanol were purchased from Merck & Co. Chemical. Sample of palm oil was purchased from local store on Indonesia.

Preparation and characterization of Ca(OH)₂/KF

Amount of natural Ca(OH)₂ mixed KF with molar ratio of Ca(OH)₂ to KF was 0.8:1. The mixture was ground by mortar until evenly for 15 minutes. The homogenous mixture was added by 3 mL of distilled water then it was pulverized by mortar for 15 minutes. The resulted sludge was dried up at 120 °C for 6 hours. The dried sludge were crushed and filtered with 100-mesh sieve. The amount of 7 g powder was calcined at 400, 500, and 600 °C for 10 min. by heating rate of 200 °C/min. on rapid thermal annealing (RTA) furnace (Figure 1).

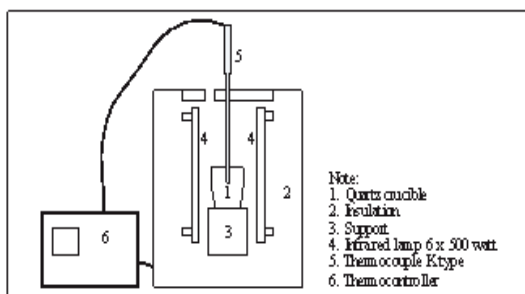


Fig. 1. RTA furnace

Powder XRD patterns were recorded on a Shimadzu XRD 6000 diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 30 mA. An FTIR spectrum of the catalyst was detected by using Shimadzu IR Prestige 21 spectrophotometer. Basic strength of catalyst was detected by CO_2 -TPD on Thermo Scientific TPDRO 1100. Thermal decomposition of catalyst was investigated by TGA on Linseis STA PT1600. The surface area was detected by Quantachrome Nova 1200. The best character was chosen for variation of $\text{Ca}(\text{OH})_2$ to KF mol ratio. The variations were 0.8:0.5, 0.8:1, and 0.8:1.5. They were characterized by XRD, FTIR, CO_2 -TPD, TGA, and surface area analyzes. The obtained catalyst is abbreviated in Table 2.

Table 2: Abbreviation of catalyst

Mol $\text{Ca}(\text{OH})_2$	Mol KF	Calcination temperature	Abbreviation
0.8	0.5	500	CaK-A-500
0.8	1	500	CaK-B-500
0.8	1.5	500	CaK-C-500
0.8	1	400	CaK-B-400
0.8	1	600	CaK-B-600

Transesterification of palm oil

The transesterifications were conducted at 65 °C. Experiments were carried out in a 50 mL of three-necked flasks (Fig. 2). Catalysts and methanol were mixed in advance at room temperature for 15 minutes. Then the mixture was heated at 65 °C. In a separate container, palm oil was heated at temperature of 65 °C. This reaction set up by mixing all the reactants and catalysts at 65 °C. The molar ratio of palm oil to methanol was maintained at 1:12. The catalyst used was 5 % by weight of oil. After each reaction, the catalyst was separated by using a centrifuge at 15,000 rpm for

30 second. The methyl esters were investigated at various reaction times. The investigation used Agilent of 400 MHz H-NMR Spectrometer. Conversion of palm oil to biodiesel can be measured based on Knothe's method¹³ from integration values of glyceridic and methyl ester protons in H-NMR.

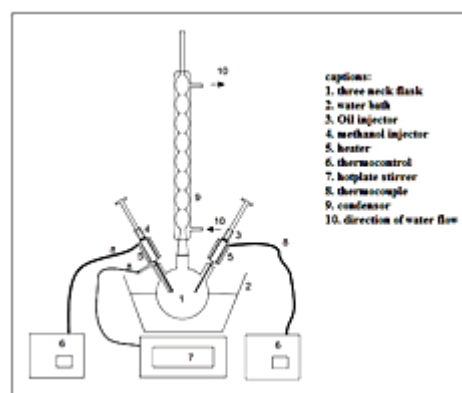


Fig. 2. Transesterification reactor

RESULTS AND DISCUSSION

Characterization of Catalyst

X-ray Diffraction, Fig. 3 depicts the profiles of natural $\text{Ca}(\text{OH})_2$ and dried natural $\text{Ca}(\text{OH})_2$ -KF mixture. Fig. 3a represents natural $\text{Ca}(\text{OH})_2$ containing CaCO_3 impurities. Concentration of $\text{Ca}(\text{OH})_2$ and CaCO_3 in natural $\text{Ca}(\text{OH})_2$ will be discussed on TGA session. The XRD profile of the dried $\text{Ca}(\text{OH})_2$ -KF mixture is shown in Fig. 3b. This reflects that KCaF_3 has been formed on this stage in small quantities. The KCaF_3 formed in 2 phases was monoclinic and orthorhombic. KCaF_3 crystals are very clear when the mixture is calcined. At calcination of 500 °C, CaK-A-500 and CaK-C-500 indicates an imperfect reaction (Fig. 4). On the XRD profile, the peaks of $\text{Ca}(\text{OH})_2$ and CaCO_3 apparently remains to have high intensity. The imperfection of reaction on CaK-A-500 was caused by deficiency of K atoms. Another case in CaK-C-500, the possibility of this imperfection due to hygroscopic catalyst was fairly high. The best catalyst was CaK-B-500 in its XRD profile, the peaks of $\text{Ca}(\text{OH})_2$ and CaCO_3 were low, but the one with KCaF_3 was elevated. The monoclinic KCaF_3 peaks appear at 2θ 20.08, 28.6, 40.93, 51.01, and 59.54 degrees¹⁴. The orthorhombic KCaF_3 peaks come out at 2θ 35.54, 37.17, 48.10, and 68.23 degrees¹⁵. KCaF_3 monoclinic formation was also reported by Fan⁹ in

a conventionally calcined Ca(OH)_2 -KF reaction. Furthermore, the CaK-B-500 catalyst was selected for variations of calcination temperature. Profile of XRD in Fig. 5 indicates that monoclinic and orthorhombic KCaF_3 peaks turn up. The higher the calcination temperature was, the peak intensity of Ca(OH)_2 d_{101} (2θ 33.8 deg) was dropped off. A decrease of intensity also occurred in CaCO_3 . It can be confirmed by TGA (Fig. 8) and FTIR (Fig. 6). This phenomenon proves that KF is not only reactive to Ca(OH)_2 but KF is also reactive to CaCO_3 . Thus this is the first paper postulated that KF can be reactive to CaCO_3 . Reaction between KF and CaCO_3 produces orthorhombic KCaF_3 . The equation of the reaction is written as follows:

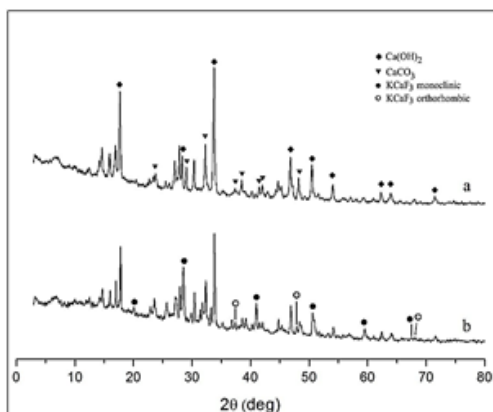
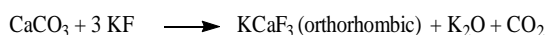
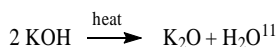


Fig. 3. Diffractogram a) natural Ca(OH)_2 , b) mixture of Ca(OH)_2 -KF

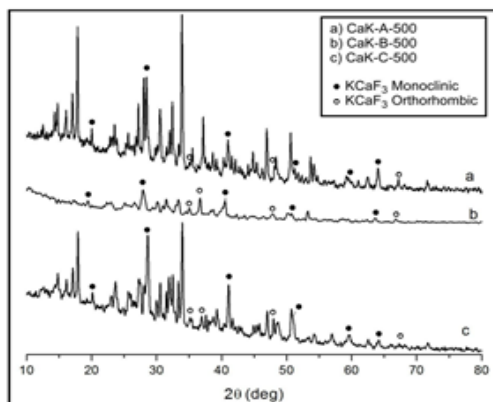


Fig. 4. XRD profile of catalysts at various molar ratios of Ca(OH)_2 to KF

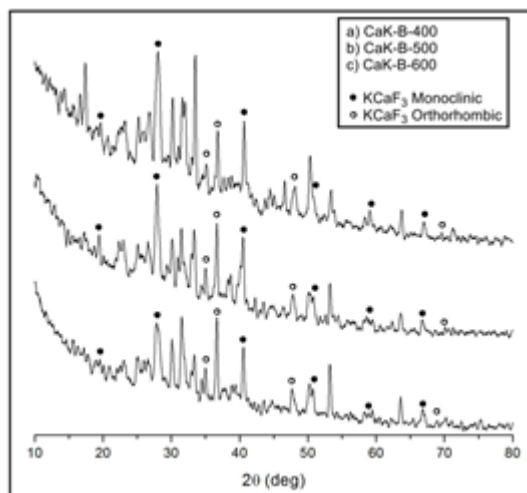


Fig. 5. XRD profile of catalysts at various calcination temperatures

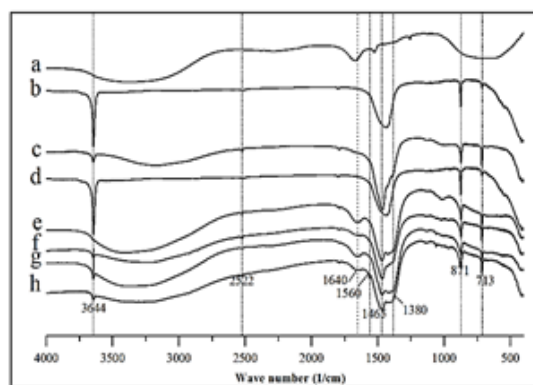


Fig. 6. FTIR Spectra of catalyst, a) KF, b) natural Ca(OH)_2 , c) dried mixture of Ca(OH)_2 -KF (CaK-B-500 °C before calcination), d) CaK-A-500, e) CaK-C-500, f) CaK-B-400, g) CaK-B-500, h) CaK-B-600

Fourier Transform Infrared (FTIR)

Figure 6 depicted FTIR spectra for KF, natural Ca(OH)_2 , dried natural Ca(OH)_2 -KF mixture, and catalysts after calcinations. Fig. 6a is a spectrum of KF. The KF spectrum is similar to pure water spectrum. It indicates that KF does not absorb IR rays and KF is highly hygroscopic. On Fig. 6a-6h, broadband at 2600-3600 cm^{-1} is vibration of O-H in water and 1640 cm^{-1} corresponding to bending mode of H_2O ¹⁶. Vibration band at 3644 cm^{-1} was corresponded to O-H bond of Ca(OH)_2 ¹⁷. Peak height at 3644 cm^{-1} was corresponded to Ca(OH)_2 concentration. The study of Ca(OH)_2 concentration will be discussed at TGA session. The vibration band 1465, 1389, 873, 713 cm^{-1} correspond to vibration modes on CaCO_3 ¹⁷⁻¹⁹.

Surface area and CO₂-TPD, Based on the data from nitrogen adsorption isotherms (Table 3), the catalysts were micro-porous material. The best of surface area catalyst was CaK-B-500 with surface area of 21.81 m²/g and pore diameter 1.18 nm. Character of CO₂ desorption for all synthesized catalyst have superbase sites. On the data CO₂-TPD (Fig. 7), CO₂ desorption was occurred on 550 – 950°C. The order of basic strength is CaK-B-500 > CaK-B-600 = CaK-B-400 > CaK-C-500 > CaK-A-500. The CaK-B-500 is the best basic

strength. It has two CO₂-TPD peaks on 900 and 950 °C. Having compared with KF/CaO that synthesized by Lin²⁰, the CaK-B-500 seems more superior. Basic strength of KF/CaO that synthesized by Lin was 600-700 °C. The high of the catalyst basic strength is derived from KCaF₃⁵ and K₂O²¹ compounds. At Table 3, the catalyst has almost the same base. Therefore, the basic strength is very influential on catalytic ability. In this case, the CO₂ detected by the TPD instrument comes from the base sites and decomposition of CaCO₃, but desorption of CO₂ from the decomposition was very small.

Table 3: Absorption isotherm and basicity of the catalyst

Catalyst	Surface area (m ² /g)	Pore diameter (nm)	CO ₂ from decomposition CaCO ₃ (mmol /g) ^a	Basic strength (mmol/g) ^b
Natural Ca(OH) ₂			1.86	Not investigated
CaK-A-500	15.19	1.19	0.56	2285.18
CaK-B-500	21.81	1.18	0.19	2125.77
CaK-C-500	16.79	1.19	0.02	2381.20
CaK-B-400	12.48	1.19	0.18	2095.40
CaK-B-600	14.88	1.19	undetected	1902.47

^aData from TGA

^bData from CO₂-TPD

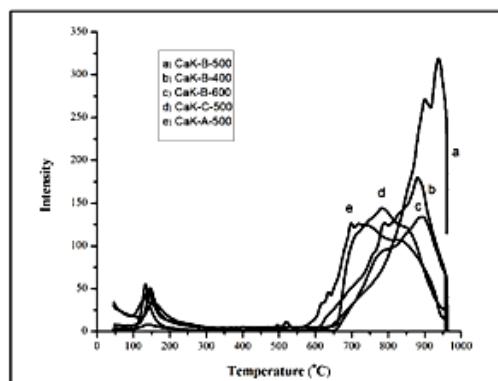


Fig. 7. Desorption of CO₂ from the catalyst

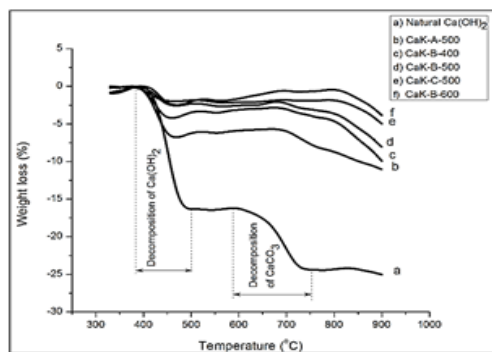


Fig. 8. Thermogravimetry analysis of the catalyst

Thermogravimetry analysis. Based on XRD data, the natural Ca(OH)₂ contains Ca(OH)₂ and CaCO₃. Based on XRD data, natural Ca(OH)₂ contains Ca(OH)₂ and CaCO₃. The Ca(OH)₂ and CaCO₃ concentrations can be measured based on TGA data. Fig 8, weight loss at temperature of 380-500 °C indicates decomposition of Ca(OH)₂ to CaO and H₂O. The weight loss at 590-750 °C represents decomposition of CaCO₃ to CaO and CO₂. The decomposition of Ca(OH)₂ and CaCO₃ at this approaching temperature were also reported in other paper²²⁻²⁶. Concentration of Ca(OH)₂ and CaCO₃ were represented on Fig. 9 and Fig.10. In Fig. 9, the higher the calcination temperature, the concentration of Ca(OH)₂ and CaCO₃ dropped off. This fact indicates that the higher temperature leads to an increase in reaction rate. The decrease of Ca(OH)₂ and CaCO₃ proves that both can be reactive to KF. In Fig. 10, an increase in KF concentration results in a decrease in Ca(OH)₂ and CaCO₃ concentrations. It means that an increase in concentration of the reactants will speed up the reaction rate. This phenomenon fits the law of the reaction rate. These data fit with XRD and FTIR data.

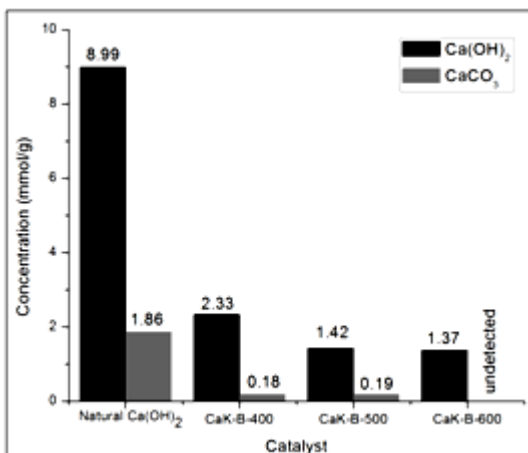


Fig. 9. The decrease of Ca(OH)₂ and CaCO₃ on CaK-B catalyst based on TGA

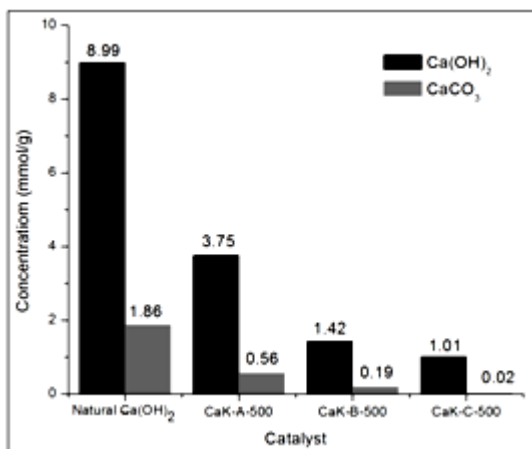


Fig. 10. The decrease of Ca(OH)₂ and CaCO₃ on CaK catalyst at 500 °C based on TGA

Transesterification of palm oil. Fig. 11, palm oil has been widely converted in 1 minute. The activity of catalyst CaK-B-500 is better than the one with CaK-B-400 and CaK-B-600 catalyst. In 1 min. CaK-B-500 catalyst can convert palm oil to methyl ester by 97.6 %. In Fig. 12, activity of CaK-B-500 catalyst is better than the one with CaK-A-500 and CaK-C-500 catalyst. This phenomenon suits perfectly with the data of the surface area and basic strength. The CaK-B-500 catalyst has the best surface area and strength characteristics. When CaK-B-500 catalysts are compared with a homogeneous catalyst for transesterification²⁷⁻²⁹, the CaK-B-500 catalyst activity is superior. So the catalyst is potential to be used in the flow reactor.

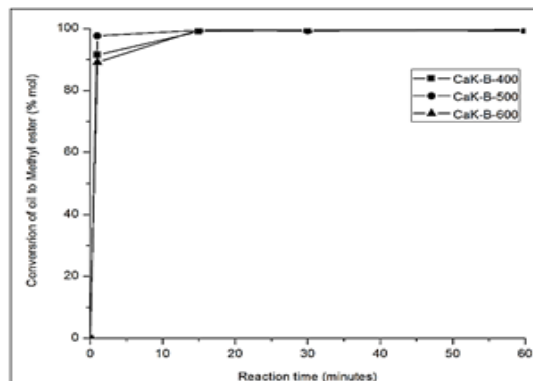


Fig. 11. Transesterification of palm oil used catalyst CaK-B. Mol ratio oil to methanol 1 : 12, temperature reaction 65 °C, weight of catalyst 5 % from weight of oil

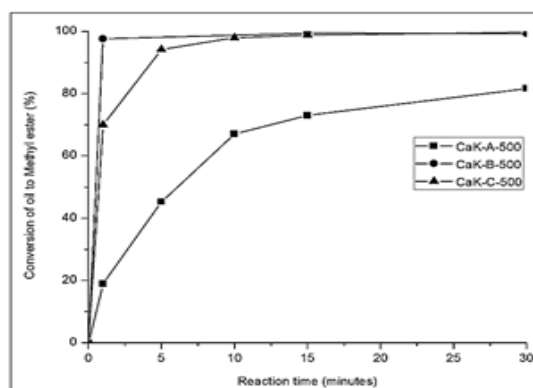


Fig. 12. Transesterification of palm oil use catalyst CaK-A-500, CaK-B-500, and CaK-C-500 . Mol ratio oil to methanol 1 : 12, temperature reaction of 65 °C, weight of catalyst of 5 % from weight of oil

CONCLUSION

A natural Ca(OH)₂ containing CaCO₃ impurities can be reactive to KF in order to create monoclinic and orthorhombic KCaF₃. The Monoclinic KCaF₃ is formed from reaction between Ca(OH)₂ and KF. The orthorhombic KCaF₃ is formed from the reaction between CaCO₃ and KF. The natural Ca(OH)₂/KF catalyst can be used as an effective catalyst for transesterification of soybean oil and methanol. Under optimum conditions, natural Ca(OH)₂/KF catalyst can convert 97.6 % of palm oil into biodiesel.

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