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Submission date: 30-Oct-2020 05:38AM (UTC+0700)

Submission ID: 1430612394

File name: geneous_Catalyst_for_Transesterification_of_Palm_Cooking_Oil.pdf (505.99K)

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Character count: 16246

Cement Kiln Dust as Heterogeneous Catalyst for Transesterification of Palm Cooking Oil

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Abstract: Cement kiln dust (CKD) is alkaline materials which contains solid material mixture mainly calcium oxide (CaO). The activation process of CKD was carried out with refluxing methanol at T 343.15 K for 90 minutes. The activation studies were performed based on methanol to oil weight ratio (1:1, 3:1, and 5:1). The transesterification performance studies were carried out in intensified reactor at T 343.15 K and 353.15 K with various methanol to oil mole ratios (200:1 and 300:1). It is found that CKD was activated at temperature of 340.15 – 355.15 K. Therefore, the use of CKD catalysts for transesterification at temperatures higher than 355.15 K will not be effective. Furthermore, it is suggested that the activation process should not be performed for a longer time than 30 min. Transesterification with high methanol to oil mole ratios (200:1 and 300:1) showed a good performance at 353.15 K. Both ratios achieved >98% yield of ME in 40 minutes. Nevertheless, the reversible reaction must be considered in the whole process. The performance of activated CKD as catalyst on transesterification of palm cooking oil is significant compared with the original CKD. This research confirmed that activated CKD is a potential heterogeneous catalyst for transesterification process.

Keywords: activation; calcium methoxide; calcium oxide; cement kiln dust; heterogeneous catalyst; methanol; mole ratio; temperature; transesterification

Date of Submission: 28-08-2019

Date of Acceptance: 12-09-2019

I. Introduction

Biodiesel can be produced with several technological processes. The most commonly used technology is transesterification of triglycerides with short-chain alcohols such as methanol using homogeneous alkaline catalysts [1]. The transesterification of vegetable oil catalyzed with sodium hydroxide (NaOH) was completed in one hour reaction has been reported by Freedman et al. [2]. Basic catalytic process is superior to acid catalytic process e.g. sulfuric acid (H₂SO₄) in catalyzing transesterification reaction [3,4]. Nevertheless, the homogeneous basic catalytic process has several drawbacks.

The use of homogeneous catalysts for transesterification has disadvantages in terms of complex separation, purification, and its selectivity which depends on FFA content of feedstock. Furthermore, the labor and materials required for neutralization, separation, and removal of the catalyst create economic and environment concerns. Therefore, the study on heterogeneous catalysts is becoming more interesting due to simpler separation process and various raw materials offered.

The development of solid base catalyst from various metal oxides such as magnesium methoxide, calcium oxide, calcium alkoxide, and barium hydroxide are studied to encounter the drawbacks of homogeneous catalyst. However, these catalysts have little or no recyclability due to solubility of solid metal oxide and hydroxides in methanol. Hence, efficient, viable, and environmentally friendly catalyst for biodiesel production needs to be developed.

One of the potential materials that can be utilized as heterogeneous catalyst is cement kiln dust. CKD is a waste material from cement industries that has not been utilized efficiently yet. This material consists of fine particles collected by the ash collection system in the cement production process. CKD particle sizes range from 0.1 to 100 microns, and has a specific gravity between 2.6 and 2.8 [5]. This material contains a particulate mixture of partially calcined materials and unprocessed draw materials, clinker ash, ash fuels, sulfates, halides, and other volatile materials.

Composition of CKD according to Lin et al. [6] consist of various oxides mainly calcium oxides (CaO), alumina (Al₂O₃), ferroxides (Fe₂O₃), and silica (SiO₂). Lin et al. [6] reported this material has been found to be economical and environmentally friendly catalyst which can catalyze esterification reactions and/or transesterification reactions.

The potential of CaO as a catalyst for transesterification process has been reported by Kouzu et al. [7]. The use of CaO as a catalyst produces the highest yield compared with other forms of calcium compounds such

as calcium hydroxide ($\text{Ca}(\text{OH})_2$) or calcium carbonate (CaCO_3). Kawashima et al. [8] reported that CaO was active and could yield 90% biodiesel from transesterification of rapeseed oil with methanol within 3 hours reaction. The effect of moisture on catalytic activity of CaO was explored by Liu et al. [9].

The study presented in this paper focused on the activation of local CKD for transesterification process. The local CKD characterized and activated using methanol with various weight ratios and activation times. The activated CKD performance was compared with original CKD in transesterification process of palm cooking oil with methanol.

II. Material And Methods

Materials:

A commercial palm oil cooking oil from supermarket (with FFA = 0.08% max) is used as the main material in this project. The methanol pro analysis quality (99.8%) provided by PT. Smart Lab Indonesia is utilized as the reactant. CKD is kindly provided by private cement factory PT. Indocement Tunggal Prakarsa, Tbk.

Methods:

Characterization of CKD

Cement kiln dust was characterized to identify its contents. The compositions of CKD were analyzed using Energy Dispersive X-Ray Spectrometer (EDS) (JED-2300T, JEOL, USA).

Catalyst Activation Study

CKD was activated by contacting CKD with methanol at 343.15 K (reflux temperature) for 45 to 90 minutes. The activation studies were performed based on methanol to CKD weight ratio (1:1, 3:1, and 5:1). The sample was taken every 15 minutes for further characteristic analysis.

Catalyst activation studies include analysis of changes in chemical compounds and chemisorption analysis. The chemical compounds changes were analyzed using Fourier transform infrared spectroscopy (FTIR) (IRTracer-100, Shimadzu, Japan) and x-ray diffractometer (XRD) (ADX-2500, Angstrom Advanced Inc., USA). The chemisorption of catalyst were analyzed using Chemisorptions analyzer (Auto Chem II 2920 series V4.04, Micromeritics Instrument Corp., USA).

Catalytic Experiments

The activated CKD performance as heterogeneous catalyst was investigated for transesterification reaction in an intensified reactor system (i.e. a combination of cavitations reactor and static mixer) as shown in Fig. 1.

The amount of methanol and palm cooking oil used in the experiments was calculated based on methanol to oil mole ratio (200:1 and 300:1). Then, the amount of catalysts calculated based on the weight of oil used i.e. 4 wt%.

As much as 4 wt% CKD was added to the reactor with methanol prior to esterification process. The resulting suspension was flowed through the reactor system with a flow rate 60 LPM for 30 minutes at refluxing temperature (343.15 K) to activate the catalyst. Afterwards, the palm cooking oil was added to the catalyst composition mixture. The reaction continued at 343.15 K for 80 minutes.

Samples were taken from the reaction mixture every 20 minutes. The biodiesel product, namely fatty acid methyl esters (FAME) which soluble in methanol, was then isolated from the mixture using simple filtration. At the final stage, FAME and methanol was separated using a rotary evaporator. Separated FAME products were analyzed using proton nuclear magnetic resonance ($^1\text{H-NMR}$) (JEOL ECS-400, JEOL, USA) in deuterated chloroform (CDCl_3). The $^1\text{H-NMR}$ analysis used to determine the conversion of TG to ME. This method is validated by Knothe [10] as suitable analysis method for transesterification monitoring and biodiesel fuel quality assessment.

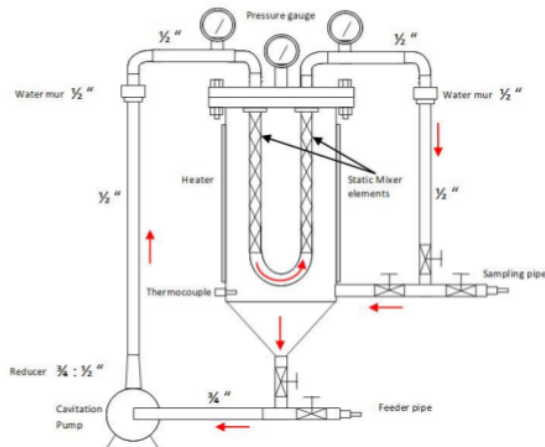


Figure 1 The schematic of intensified reactor.

III. Result and Discussion

Characterization of CKD

The chemical composition of local CKD and common CKD reported by Lin et al. [6] are shown in Table 1. The composition different from common CKD reported by Lin et al. [6] was the absence of sodium oxides (Na₂O), potassium oxides (K₂O), and sulphite (SO₃) contents.

Table 1 Chemical compositions of CKD

Component	Reported by Lin et al. [6]	Analysis
	Mean (wt%)	(wt%)
SiO ₂	15.05	4.74
Al ₂ O ₃	4.43	8.94
Fe ₂ O ₃	2.23	2.83
CaO	43.99	56.52
Na ₂ O	0.69	-
K ₂ O	4.00	-
MgO	1.64	1.47
SO ₃	6.02	-

The composition of CKD used in this project is dominated by CaO (56.52%). Therefore, the reactivity of this CKD is most likely influenced by CaO. According to Kouzu et al. [7] the mechanism of CaO as transesterification catalyst will through the stages of formation calcium methoxide. This methoxide formation reaction may occur when CaO have active sites. In this case, CKD needs to be activated using methanol.

Catalyst Activation Study

CKD were analyzed by chemisorption test to determine the activation temperature. Fig. 2 indicated that there are two points of activation temperature that detected in the original CKD i.e. 67 °C and 82 °C (340.15 K and 355.15 K) indicated the existence of strong basic sites. At higher temperature (>355.15 K), there are no active sites occur. It shows that CKD catalysts can be used as an active catalyst in the temperature range of 340.15 – 355.15 K. Fig. 2 clarify that calcium methoxide formed will be detached at a high temperature. Therefore, the use of catalysts at temperatures above 355.15 K will not be effective.

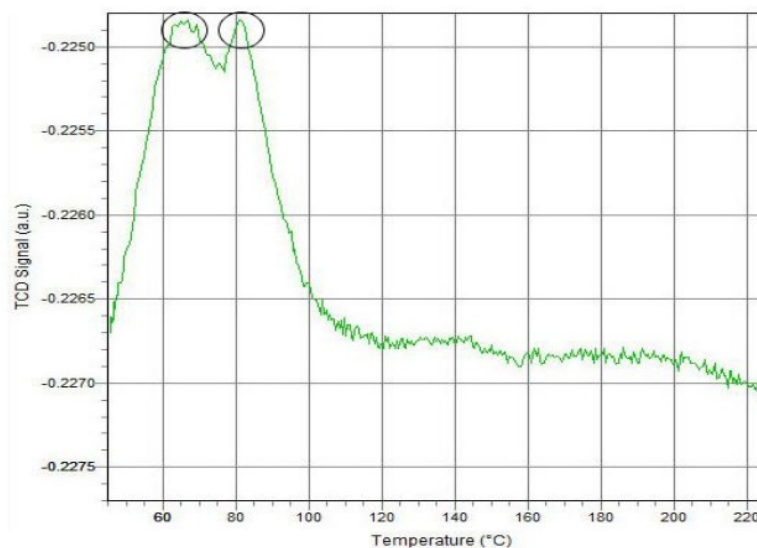


Figure 2 Chemisorptions analysis of original CKD.

Other approaches to study the effect of activation mechanism of CKD with methanol were using XRD and FTIR analysis. The results might provide clearer view if there are any chemical or physical changes.

The results of stacked XRD analysis (Fig. 3) indicate that there are no chemical changes occurred during the activation process. Methanol most likely serves as a solvent to CKD particles so that the particle orientation becomes more freely to move without having chemical reaction. The CKD still remain in solid phase after activation process.

Particles of CKD formed as disperse crystalline which are the oxides of each component. Especially the crystalline of CaO is more visible on the surface as the dominant oxide. Therefore, it will be easier for CaO to reacts with methanol at the time of the transesterification process.

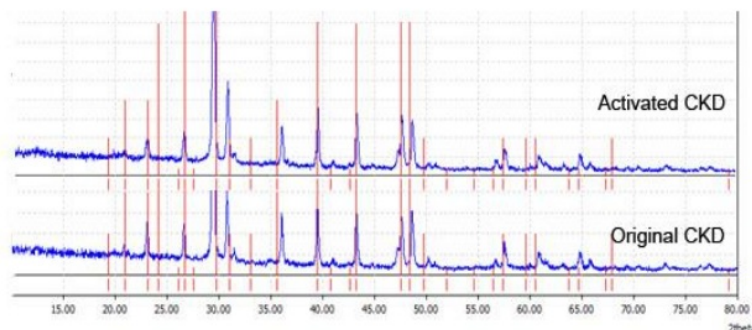


Figure 3 XRD analyses comparison between activated CKD and original CKD.

Fig. 4 shows that longer activation times did not have much effect on the formation of active sites of CKD particles. There are no chemical structures changes detected based on the results of FTIR analysis. The results confirm that the activation process of CKD only changes the crystalline structure and the particle orientation. Consequently, the calcium oxides in CKD could have more space to move for the next step of catalytic process, which is the formation of calcium methoxide.

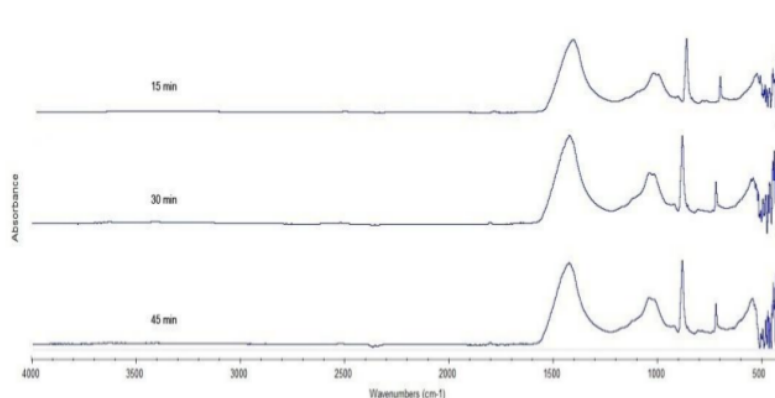


Figure 4 FTIR analyses of activated CKD based on the activation time.

Catalytic Experiments

It is essential to investigate the activation effects of CKD particles on transesterification reaction and then compared them with those of original CKD particles.

The results of activated CKD performance on transesterification is quiet significant as shown in Fig. 5. The first experiment using original CKD simultaneously with methanol and palm cooking oil demonstrated that 9.09% TG converted to ME after 30 min of reaction. On the other hand, 95.63% conversion of TG to ME was achieved when CKD was activated first prior to transesterification reaction. This reactivity difference can be attributed to evenly suspended CKD particles in methanol that provide a high area of contact and the formation of calcium methoxide as active catalyst.

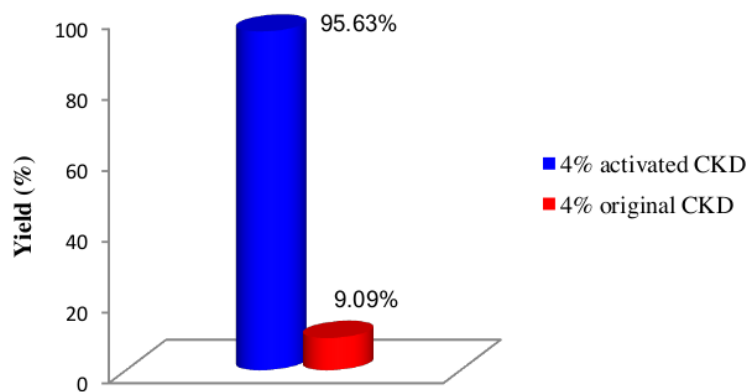
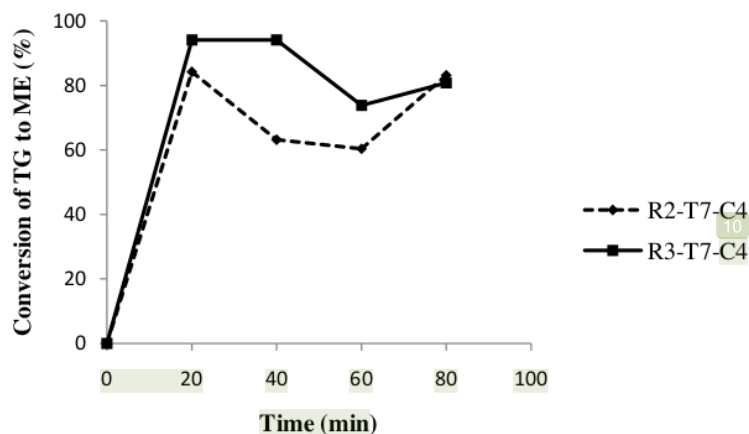


Figure 5 Yield comparison between transesterification with 4 wt% activated CKD and transesterification with 4 wt% original CKD.

Activated CKD performance was also tested on transesterification of palm cooking oil with methanol at various temperatures and with various mole ratios of methanol to oil.

Fig. 6 demonstrated the conversion of TG to ME for transesterification of palm cooking oil at T 343.15 K in the presence of 4 wt% CKD catalysts. In the first 20 minutes, the conversion of TG to ME reached >84% for both mole ratio of methanol to oil (200:1 and 300:1). After 40 minutes reaction, the conversion is decreased and continued until 60 minutes of reaction. The conversion of TG to ME was begun increasing again after passing a reaction time of 60 minutes. This suggests that the rapid production of FAME also produce glycerol which can lead to reversible reaction occurred. Nevertheless, the reversible reaction rate of the transesterification reaction is slower than the reaction rates of TG to ME. Fig. 7 illustrated the reversible reaction of transesterification in the presence of glycerol and FAME.



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Figure 6 Conversion of TG to ME for transesterification of palm cooking oil:
R2T7C4 = methanol to oil mole ratio (200:1), T 343.15 K and 4 wt% CKD.
R3T7C4 = methanol to oil mole ratio (300:1), T 343.15 K and 4 wt% CKD.

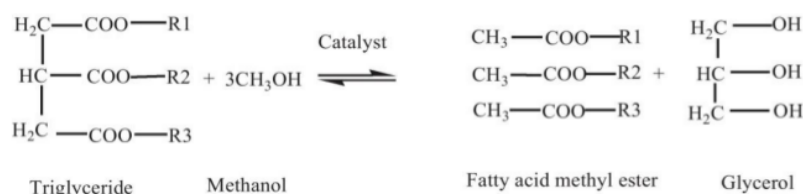


Figure 7 Transesterification of TG with methanol for production of FAME.

The conversion of TG to ME for transesterification of palm cooking oil at T 353.15 K in the presence of 4 wt% CKD catalyst demonstrated higher conversion as showed in Fig. 8. Especially for methanol to oil mole ratio 300:1 achieved 100% conversion of TG to ME in the first 20 minutes and continued constant. The conversion of TG to ME for methanol to oil ratio 200:1 showed slower conversion in the first 20 minutes. At higher temperature (353.15 K) and with a small ratio of the amount of methanol in the reactor, methanol was evaporated quickly into the vapor phase. The evaporation of methanol resulted in low formation of calcium methoxide as the active catalyst and led to slower conversion. After 40 minutes reaction, the methanol has reached equilibrium between vapor phase and liquid phase. As a result, the conversion of TG to ME increased significantly to 98.8%. After 60 minutes reaction, the conversion was decreased due to reversible reaction.

To overcome reversible reaction, in addition to using excess methanol over the stoichiometric amount, can be accomplished by either collecting main product (FAME) or separating glycerol continuously from the reactor.

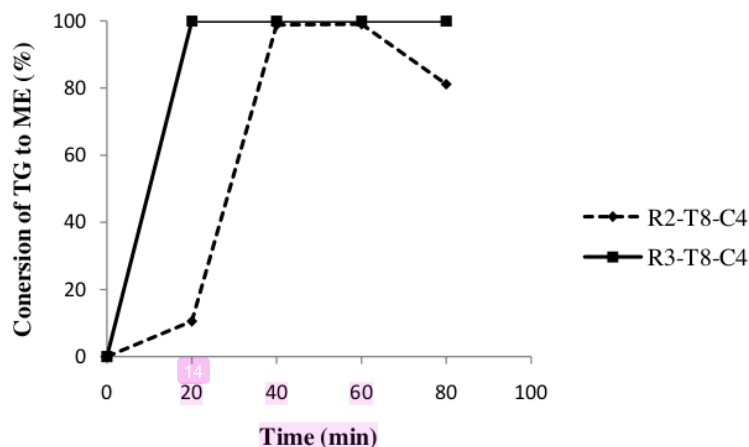


Figure 8 Conversion of TG to ME for transesterification of palm cooking oil:
 R2T8C4 = methanol to oil mole ratio (200:1), T 353.15 K and 4 wt% CKD.
 R3T8C4 = methanol to oil mole ratio (300:1), T 353.15 K and 4 wt% CKD.

IV. Conclusion

The CKD utilized was characterized as a mixed fine particle with several reactive basic oxides. CaO was the dominant component with the absence of Na₂O, K₂O, and SO₃ content. It is found that CKD was activated at temperature range from 340.15 – 355.15 K. Therefore, the use of CKD catalysts for transesterification at temperatures higher than 355.15 K will not be effective. Longer activation time has no significant effect on the catalyst. Hence, it is suggested that the activation process should not be performed for a longer time than 30 min. Transesterification with high methanol to oil mole ratios (200:1 and 300:1) showed a good performance at temperatures 353.15 K. Both ratios achieved >98% yield of ME in 40 minutes. Nevertheless, the reversible reaction must be considered in the whole process. The performance of activated CKD as catalyst on transesterification of palm cooking oil is significant compared with the original CKD. This research confirmed that activated CKD is a potential heterogeneous catalyst for transesterification process.

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Wahyudin. " Cement Kiln Dust as Heterogeneous Catalyst for Transesterification of Palm Cooking Oil." *IOSR Journal of Applied Chemistry (IOSR-JAC)* 12.9 (2019): 01-07.

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