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by Joelianingsih Joelianingsih

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Characterization and Activation of Cement Kiln Dust as Heterogeneous Catalyst for Transesterification Process

Wahyudin^{1,2}, Joelianingsih¹, Hiroshi Nabetani², Nanik Purwanti³,
and Armansyah H. Tambunan^{3*}

¹Department of Chemical Engineering

Institut Teknologi Indonesia, Serpong 15320 Indonesia

²International Program in Agricultural Development Studies

The University of Tokyo, Tokyo 1138657 Japan

³Department of Mechanical and Biosystem Engineering

Bogor Agricultural University, Bogor 16002 Indonesia

Email: ahtambun@ipb.ac.id

Abstract. Cement kiln dust (CKD) is a fine, solid material, highly alkaline waste mainly reactive calcium oxide. The characteristic of local CKD is slightly different to most other CKD in general, especially the absence of sodium oxide, potassium oxide, and sulphite content. Therefore, calcium oxide is the dominant basic oxide (56.52 wt. %) that influence the activity of CKD as catalyst. Analysis of activated CKD with FTIR and XRD showed no chemical reaction occur during activation stages. Furthermore, SEM analysis demonstrated that particle structures of activated CKD are more freely dispersed compared to fresh CKD. Surface area of activated CKD is enhanced, and slightly decrease on longer activation time. In correlation with the later, particle size analysis and density analysis showed swelling process occur that cause a decrease in surface area. Activated CKD performance on transesterification is significant compared to fresh CKD. Results showed that 9.09% methyl ester (ME) conversion were obtained when feedstocks were added simultaneously with fresh CKD, whereas 95.63% ME conversion was obtained when CKD was activated prior to transesterification. This reactivity difference can be attributed to the occurrence of evenly suspended CKD in methanol to provide a high area of contact.

Keywords: activation; calcium oxide; catalyst; cement kiln dust; transesterification.

1 Introduction

Vegetable oil into one of the natural resources that get more attention as a feedstock in biodiesel production to reduce exhaust emissions. Biodiesel production process is currently underway with several technological processes. The technology most commonly and frequently used is the transesterification of triglycerides with short-chain alcohols (low Mass Relative/MR) such as methanol using homogeneous alkaline catalysts [1]. This reaction is relatively inexpensive for moderate reaction conditions. The transesterification of



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vegetable oil catalyzed with NaOH was completed in 1 hour reaction has been reported by Freedman et al. [2]. While sulfuric acid has also the ability in catalyzing the transesterification reaction, the acid catalytic process is significantly slow compared to basic catalytic process [3,4]. Nevertheless, the later reaction is very limited to raw material with low free fatty acids (FFA).

The use of homogeneous catalysts have disadvantages in terms of separation and selectivity also depends on FFA content used as feed. Consequently, the labor and materials required for the neutralization, separation, and removal of the catalyst creates economic and environment concerns. Therefore, heterogeneous catalysts are more preferable due to simpler separation process and various raw materials offered.

In order to circumvent the drawbacks of homogeneous catalysts, researchers try to find better solution by developing solid base catalyst from various metal oxides such as magnesium methoxide, calcium oxide, calcium alkoxide, and barium hydroxide. However, these catalysts have little or no recyclability due at least in part to the solubility of solid metal oxide and hydroxides in methanol. Therefore, efficient, viable, environmentally friendly catalyst for biodiesel production is needed to be developed.

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

Until now CKD waste has not been used optimally yet especially in Indonesia. On a scale of cement plant, CKD used as supplementary feed entered as recycled materials, but can only be done one time only, after that it was discarded as waste. Other uses under study is more focused on concrete industrial buildings and roads. The content of oxides in the CKD can strengthen concrete roads, buildings and structures at low cost. However, its use is still limited and still needs further research.

Characteristic of CKD according to Lin et al. [6] consist of various oxides mainly calcium oxides, alumina, ferroxides, and silica. Lin reported this material has been found to be economical and environmental friendly catalyst which can catalyzed esterification reactions and/or transesterification reactions. CKD can also be used several times in biodiesel process to more than 16 times.



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Our interests in this paper were concentrated on the activation of local CKD as heterogeneous catalyst for transesterification process since there are no work describing the effects of CKD activation so it can be used as a catalyst. In this paper, the local CKD characterized and activated by using methanol with various weight ratio and activation time. Activated CKD were tested and compared with fresh CKD in transesterification process on palm cooking oil with methanol.

2 Experimental

2.1 Characterization of CKD

Cement kiln dust from the factory was characterized first especially to identify the free oxides content in the CKD. The structure of how particles positioned in CKD also analyzed to have the overview of the effect of activation process. Sometimes the particles stack together physically which make difficult to react with other chemical reactant, i.e. methanol in this case, to form methoxide.

The characterization of CKD was conducted by using Energy Dispersive X-Ray Spectrometer (EDS) JED-2300T. The structure of CKD particles was analyzed by using Scanning Electron Microscopy (SEM) SU70 in addition to EDS analysis.

2.2 Catalyst Activation Study

Cement Kiln Dust (CKD) was activated by contacting with methanol at reflux temperature (65 °C) and mixed for 15 – 45 minutes. The activation study were performed based on methanol to oil weight ratio (1, 3, and 5).

The activated CKD catalyst were analyzed by using SEM SU70, X-ray diffractometer (XRD) ADX-2500, Fourier transform infrared *spectroscopy* (FTIR) IRTracer-100 Shimadzu, Particle size analyzer (PSA) CILAS 1190, BET surface area analyzers Quantachrome instruments NOVA Series V11.03.

2.3 Catalytic Experiments

A typical procedure for the transesterification reaction was conducted for catalytic experiments in this study. Methanol with 300 mole ratio was added to 4 wt. % CKD concentration (based on oil weight), and the resulting suspension was flowed through the reactor system with flow rate 60 LPM for 30 minutes under refluxing conditions (65 °C) to activate the catalyst. Afterwards, the palm cooking oil as much as mole ratio calculated is added to the catalyst composition mixture. The reaction then continued under temperature condition 70 °C.



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Sample aliquots withdrawn from the reaction mixture at time intervals of 15 – 30 minutes. Biodiesel product (FAME) then isolated from the mixture by using simple filtration and centrifuge, and for the final stages FAME and methanol were separated in rotary evaporator. Separated FAME products were analyzed by ¹H NMR in CDCl₃.

3 Results and Discussion

3.1 Characterization of CKD

Cement kiln dust (CKD) used in this project is local material provided by private cement factory PT. Indocement Tunggul Prakarsa, Tbk. The chemical composition of this CKD as shown in Table 1 is little bit different compared to most common CKD as reported by Lin et al. [6] in Table 2, especially the absence of sodium oxide, potassium oxide, and sulphite content.

Table 1 Chemical compositions of local cement kiln dust

Component	Wt. %
SiO ₂	4.74
Al ₂ O ₃	8.94
Fe ₂ O ₃	2.83
CaO	56.52
MgO	1.47
LOI	25.5

LOI: loss on ignition

Table 2 Chemical compositions of cement kiln dust [6]

Component	Mean (wt. %)	Max (wt. %)	Min (wt. %)
SiO ₂	15.05	34.30	2.16
Al ₂ O ₃	4.43	10.50	1.09
Fe ₂ O ₃	2.23	6.00	0.24
CaO	43.99	61.28	19.40
Na ₂ O	0.69	6.25	0.00
K ₂ O	4.00	15.30	0.11
MgO	1.64	3.50	0.54
SO ₃	6.02	17.40	0.02
LOI	21.57	42.39	4.20

Kouzu et al. [7] reported the potential of calcium oxides (CaO) as catalyst for transesterification process. The use of CaO as a catalyst produces the highest yield compared to other forms of calcium compounds i.e. Ca(OH)₂ or CaCO₃. In addition, magnesium oxide (MgO) was very inactive in the transesterification process. Therefore, calcium oxide (CaO) is the dominant basic oxide that influence the activity of this local CKD as catalyst.



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3.2 Catalyst Activation Analysis

In order to understand more about the effect of activation to CKD crystalline structure, SEM analysis was carried out. The original CKD crystalline structure and orientation of materials making up the sample are closely attached and tend to overlap one another as shown in Fig. 1. This stacked orientation is physically bonded and make difficult for the active basic oxide (CaO) to react with methanol to form methoxide.

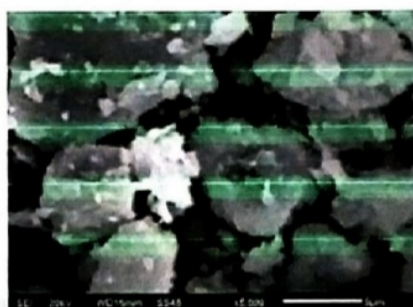


Figure 1 Fresh cement kiln dust (original)

After the activation of CKD with methanol, the crystalline structure and orientation of materials of activated CKD became more dispersed and detached each other as shown in Fig. 2. The release of the physical bond between the oxide compounds in CKD leads to activation reaction of CaO with methanol to form methoxide more easily. Therefore, the activated CKD can be used as active catalyst in transesterification process.

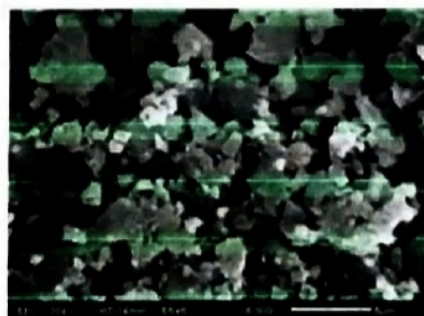


Figure 2 Activated cement kiln dust with methanol



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Another approach to study the effect of activation mechanism of CKD with methanol is by using XRD and FTIR analysis. The results would give clearer view whether there are any chemical changes or just physical effect.

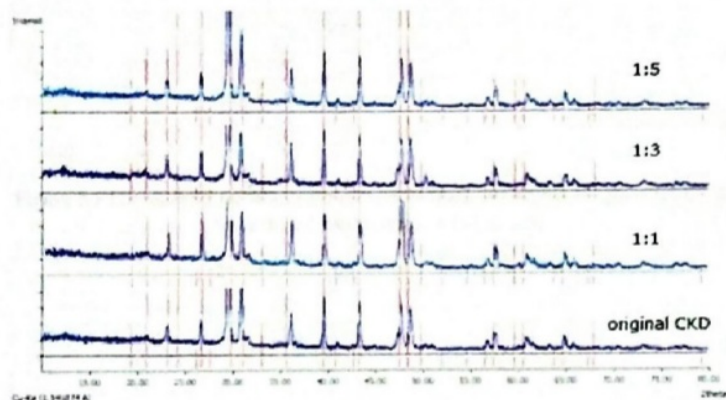


Figure 3 XRD analysis of activated cement kiln dust with various CKD to methanol weight ratio (1:1; 1:3; 1:5)

From the stacked XRD analysis results in Fig. 3, can be understood that there are no chemical changes occur during activation process. Methanol most likely serve as a solvent to CKD particles so that the particle orientation becomes more freely to move without having chemical reaction yet. It is also correspond to SEM analysis results.

To further ascertain the effect of activation process to CKD, in addition to the activation of the various weight ratios, a variation of activation time also performed. The experimental results were analyzed by using FTIR as shown in Fig. 4 to Fig. 6.

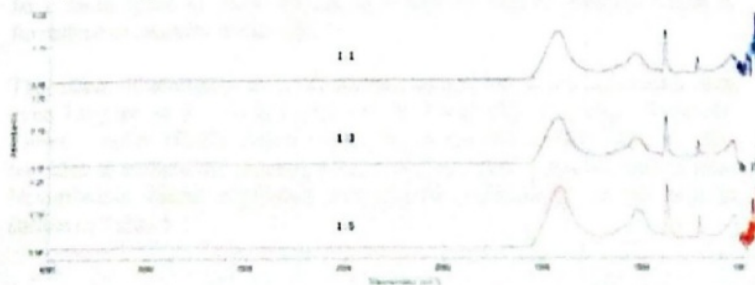


Figure 4 FTIR analysis for 15 minute activation of cement kiln dust with various CKD to methanol weight ratio (1:1; 1:3; 1:5)



Figure 5 FTIR analysis for 30 minute activation of cement kiln dust with various CKD to methanol weight ratio (1:1; 1:3; 1:5)

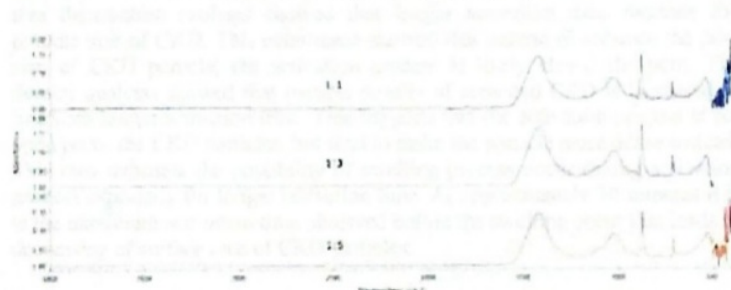


Figure 6 FTIR analysis for 45 minute activation of cement kiln dust with various CKD to methanol weight ratio (1:1; 1:3; 1:5)

Evidently, longer activation time did not have much effect on the results of the activation of CKD based on FTIR analysis. There are no chemical structure changes detected as well as the results by XRD analysis. This confirmed that activation process of CKD is only change the crystalline structure and particle orientation so that reactive basic oxides in CKD could have more space to move for the next step of catalytic process which is formation of calcium methoxide.

The effect of methanol to CKD various weight ratios and activation time even happens to the surface area of CKD particles. By using *Brunauer, Emmett, Teller* (BET) analysis it is shown that the surface area of CKD particles is sufficiently increased from original CKD particles surface area. Nevertheless, longer activation time slightly reduced the surface area as shown in Table 3.



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Table 3 Physical characteristic of CKD

Sample	Activation Time (min)	Surface area (m ² /g)	Particle size (μm)	Density (g/cm ³)
Fresh CKD	-	2,100	7,79	3,12
Activated CKD	15	4,402	7,60	2,96
	30	4,301	8,96	3,10
	45	3,169	9,84	4,03

In order to ensure this phenomenon, further analysis is carried out. The particle size of activated CKD is approximately the same with the original CKD for the first 15 minutes of activation time. Correspond to BET surface analysis, particle size distribution analysis showed that longer activation time increase the particle size of CKD. This occurrence showed that instead of enhance the pore size of CKD particle, the activation process is likely closed the pore. The density analysis showed that particle density of activated CKD is increased in line with longer activation time. This suggests that the activation process is not open pores the CKD particles, but tend to make the particle more dense instead. This also indicates the possibility of swelling process occur during activation process especially for longer activation time. At approximately 30 minutes it is the maximum activation time observed before the swelling occur that leads to decreasing of surface area of CKD particles.

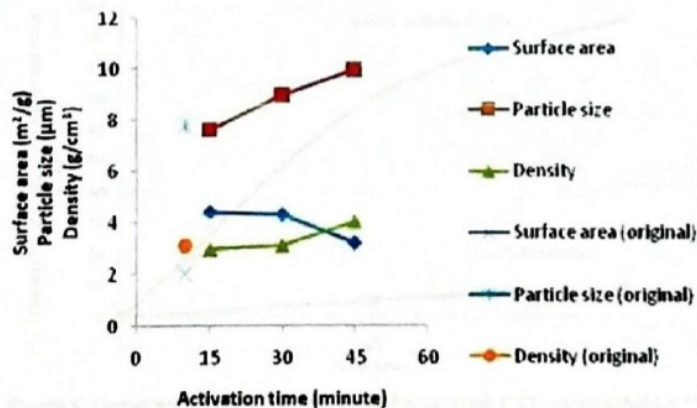


Figure 7 Analysis of activation time effect to CKD particles



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3.3 Catalytic Experiments

It is essential to investigate the activation effect of CKD particles on transesterification reaction compared to fresh CKD. In this experiment, palm cooking oil is utilized with methanol at mild conditions.

First experiment carried out by adding fresh CKD simultaneously with methanol and palm cooking oil at 70 °C. The second, CKD is activated first with methanol for about 30 minutes at 65 °C and subsequently palm cooking oil is added and the transesterification continued at 70 °C.

The products of both experiments was analyzed by using proton (¹H-NMR) analysis to determine the conversion of triglyceride (TG) to methyl ester (ME). This method is validated by Knothe [8] as suitable analysis method for transesterification monitoring and biodiesel fuel quality assessment.

Proton analysis results is quiet significant as shown in Fig. 8. The first experiment by using fresh CKD simultaneously with methanol and palm cooking oil demonstrated that 9.09% methyl ester (ME) conversion were obtained after 30 minute of reaction. While 95.63% methyl ester (ME) conversion was achieved when CKD is activated first prior to transesterification reaction. This reactivity difference can be attributed to the occurrence of evenly suspended CKD in methanol to provide a high area of contact.

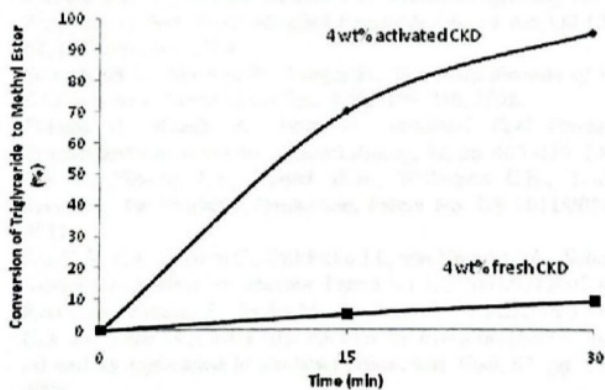


Figure 8 Conversion of triglyceride to methyl ester: fresh CKD vs activated CKD



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4 Conclusion

Local CKD was characterized as fine particle with metal oxides contained reactive basic oxide of CaO as dominant component. The characteristic of local CKD is slightly different to most other CKD in general, especially the absence of sodium oxide, potassium oxide, and sulphite content. It is understood that there are no chemical reaction changes occur during activation process. Furthermore, swelling process occur during activation process especially for longer activation time. It is suggested no activation process more than 30 minutes performed. In conclusion, activated CKD is a potential heterogeneous catalyst for transesterification process.

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6 References

- [1] Ma F., Hanna M.A., *Biodiesel Production: a review*, Bioresour Technol, 70, pp. 1–15, 1999.
- [2] Freedman B., Pryde E.H., Mounts T.L., *Variables Affecting The Yields of Fatty Esters from Transesterified Vegetable Oils.*, J Am Oil Chem Soc, 61, pp.1638-1643, 1984.
- [3] Schuchardt U., Sercheli R., Vargas R., *Transesterification of Vegetable Oils: a review*, J Braz Chem Soc, 9, pp. 199–210, 1998.
- [4] Fukuda H., Kondo A., Noda H., *Biodiesel Fuel Production by Transesterification of Oils*, J Biosci Bioeng, 92, pp. 405–416, 2001.
- [5] Cai Y., Nieweg J.A., Turner W.A., Wilkinson C.K., *Systems and Processes for Biodiesel Production*, Patent No. US 2011/0054200 A1, 2011.
- [6] Lin V.S., Cai Y., Kern C., Dulebohn J.I., and Nieweg J.A., *Solid Catalyst System for Biodiesel Production*, Patent No. US 2009/0112007 A1, 2009.
- [7] Kouzu M., Kasuno T., Tajika M., Sugimoto Y., Yamanaka S., Hidaka J., *Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production*, Fuel, 87, pp. 2798–2806, 2008.
- [8] Knothe G., *Monitoring a progressing transesterification reaction by fiber-optic near infrared spectroscopy with correlation to ¹H nuclear magnetic resonance spectroscopy*, JAOCS, 77, pp. 489-493, 2000.

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