

PROCEEDING BOOK I



CHEMMPRO 2014

MINERAL AND MATERIAL PROCESSING

International Seminar on Chemical Engineering
in conjunction with

Seminar Teknik Kimia Soehadi Reksowardojo (STKSR) 2014

"Minerals and Materials Processing Toward Sustainable Development"

Bandung, Indonesia

30 - 31 October 2014

Organized by :

Department of Chemical Engineering
Faculty of Industrial Technology
Institut Teknologi Bandung

Supported by :



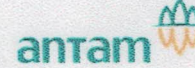
Sponsored by :



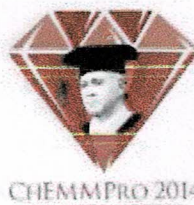
Badak LNG
A World Class Energy Company



PT FREEPORT INDONESIA
Affiliate of Freeport-McMoRan



ISSN 2354-59



October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

PREFACE

International Seminar on Chemical Engineering in conjunction with Seminar Teknik Kimia Soehadi Reksowardojo (STKSR) was held at East Hall, Institut Teknologi Bandung during 30 – 31 October 2014. This international conference had a theme of “Mineral and Material Processing” which was applicable with the enactment of Law No.4 of 2009 on Mineral and Coal Mining where the ban on the export of unprocessed minerals has been applied since January 2014. Chemical engineers hold a significant role in this area, especially to develop and implement appropriate processing technologies to the mineral resources, which also should considering the sustainable development.

There were five plenary lectures in this two-days conferences, with theme “Sustainable Mineral and Metal Processing” and “The Advancement of Chemical Engineering Technology” along with plenary discussion about “Overcome the Challenges in Indonesia’s Mineral and Materials Processing Industry”. This proceeding comprises the summary of these outstanding speech and the collected papers that has been presented in the parallel sessions. These papers are divided into several general themes: mineral processing, material processing, material refining and recovery, advance materials, nanotechnology, catalyst, polymers, and others.

The international conference provides an opportunity to publicize research works which done or in ongoing ones in many research institution and showcase their latest advancement and technologies. We have expectation in this occasion is not only a good place to exchange and discuss the progress of their research in chemical engineering that applicable to material and mineral processing, but also a venue to collect and to disseminate the most updated technologies and the researches of regional issue and public interest in order to contribute to the community and to draw support from the industrial and the governmental sectors.

We would like to grateful to all participants and sponsors who has contributed to the conference, to the organizing committee for their commitment in their busy days so that the conference is possible to be held and conducted successfully.

Thank you,

Dr. Dendy Adityawarman
Conference Chairman



CHEMMPRO 2014
INTERNATIONAL SEMINAR ON CHEMICAL ENGINEERING IN MINERALS AND MATERIALS PROCESSING

October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

COMMITTEE

Organizing committee:

Chairman	: Dr. Dendy Adityawarman
Secretary	: Dr. Dianika Lestari Dr. MTAP Kresnowati
Treasury	: Dr. Tirto Prakoso Dr. Melia Laniwati G.
Program and Papers	: Dr. Winny Wulandari Dr. IDG A. Putrawan Dr. IGBN Makertiharta Dr. Yogi Wibisono Budhi
Information and Publication	: Dr. Antonius Indarto Dr. CB. Rasrendra Dr. Ardiyan Harimawan
Logistic	: Dr. Johnner Sitompul Dr. Harry Devianto Pri Januar Gusnawan, ST, MT

Steering Committee:

Prof. Dr. Herri Susanto (ITB)
Dr. Tatang Hernas Soerawidjaja (ITB)
Dr. Tjokorde Walmiki Samadhi (ITB)
Dr. Subagjo (ITB)
Dr. Zulfiadi (ITB)
Prof. Johny Wahyuadi (UI)
Dr. Mubiar Purwasasmita (ITB)
Dr. Soemantri Widagdo
Ir. Martiono Hadiano (Newmont Indonesia)
Ir. Tato Miraza (ANTAM)
Dr. Ir. Rozik B. Soetjipto (Freeport Indonesia)

International Advisory Committee:

Prof. Dr. Tjandra Setiadi (ITB)
Prof. Geoffrey Brooks (Swinburne University)
Prof. Dr. Norikazu Nishiyama (Osaka)
Dr. Wuled Lenggoro (TUAT)
Prof. Mikrajuddin Abdullah (ITB)
Dr. Ferry Iskandar (ITB)
Prof. Dr. Ir. Rochim Suratman (ITB)

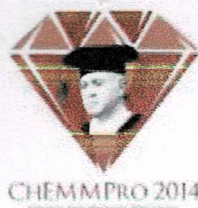


October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

TABLE OF CONTENT

PREFACE	i
TABLE OF CONTENT	ii
COMMITTEE	xi
PROGRAM	xii
KEYNOTE PRESENTATION	1
• Development of Solar Thermal Reactors for Materials Production by Ben Ekman, Prof. Geoffrey Brooks & Assoc. Prof. M. Akbar Rhamdhani	1
• Metals from Urban Ores: Opportunities, Challenges, and Technology Development by Assoc. Prof M. Akbar Rhamdhani	7
• Minerals and Materials Processing and The Challenges by Drs. R. Edi Prasodjo, M.Sc.	15
• Peran Teknologi Proses Dalam Pertambangan dan Perkembangannya di Indonesia by Ir. Hendra Santika, MM	23
• Throughput Prediction Model Development at Batu Hijau – PT Newmont Nusa Tenggara by Martiono Hadiano, Dinar Aryasena, Fattih Wirfiyata.....	29
• Direct Nickel Process – Breakthrough Technology by Graham Brock	41
• Use of Phase Diagrams for Designing Recovery Processes for Minerals and Materials by Prof. Ka Ming NG.....	51
• Assembly of Fine Particles Synthesized from the Gas-Phase by Assoc. Prof Wuled Lenggoro	59
• Shape Selectivity of MFI type Core-Shell Zeolite Catalysts by Assist. Prof. Manabu Miyamoto	75
PAPERS	89



October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

BOOK I

ADVANCED MATERIAL

Code	Title	Authors	Page
AM.01	Key Parameters to Optimize an Autoclave Technology Application for Advanced Composite Materials Processing	Handoko Subawi	91
AM.02	Effect of Bentonite Addition on Geopolymer Concrete from Geothermal Silica	Himawan Tri Bayu Murti Petrus, Joshepine Hulu, Elsa Malinda, Rizal Agung Prakosa	103
AM.03	Effect of Clay as The Catalyst in The Palm Oil Glycerolysis Process	Siti Mujdalipah, Ani Suryani, Ika Amalia K, Dewi Cakrawati	117
AM.04	The Utilization of Mineral in Crude Glycerol Purification	Siti Mujdalipah, Yatti Sugiarti, Puji Rahma N	125
AM.06	Modified Natural Zeolites for Ethanol Purification	Chandra Wahyu Purnomo, Indra Perdana, P. Sumardi	133
AM.07	Preparation of Heat-Resistant Insulator Material Advanced from Raw Materials of Silica Sand at Atmospheric Pressure	Poerwadi Bambang, Agustina Diah P, Meidiana Christia, Indahyanti Ellya	139
AM.08	Getting Capsaicin Extract from Chili Powder that Has Quality and Optimum Yield by Using The Solvent Extraction and Microwave Solvent Extraction Method	Achmad Ferdiansyah and Mahfud	147
AM.10	Utilization of Fly Ash from Coal Fired Power Plant for Zeolite Synthesis	Amelia Panca, Devina Jonathan, Dwiwahju Sasongko, Winy Wulandari	153
AM.11	Development of Silica Membrane by Sol-Gel Method for Separation of Acetic Acid and Water by Pervaporation	Samuel P. Kusumocahyo and Masao Sudoh	157
AM.12	Titanium Silicon Carbide Formation Mechanism	Solihin	171
AM.13	The Effect of Ultrasonic Radiation on Preparation Zeolite Catalyst from Natural Mineral	Widayat, H Susanto and H Satriadi	177



CHEMMPRO 2014

October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

Code	Title	Authors	Page
AM.14	A Comparative Study of Zn-ZrO ₂ Nanocomposite Coatings Obtained by Direct and Pulsed Current Electrodeposition	Marsetio Noorprajuda and Asep Ridwan Setiawan	187
AM.15	Preparation of Carbon-Based Strong Acid Catalyst by Hydrothermal Carbonization and It's Performance on Corn Starch Hydrolysis	Iryanti Fatyasari Nata, Chairul Irawan, Primata Mardina and Cheng-Kang Lee	201
AM.16	Evaluation of Erosion Resistance and Microhardness of Ni-ZrO ₂ Nano-composite Coating Fabricated by DC Electrodeposition	Jodie Ridha Arrozak, Asep Ridwan Setiawan	213

CATALYST

Code	Title	Authors	Page
CT.02	Preparation and Testing of Cu/ZnO Catalyst for Methanol Synthesis	Yusi Prasetyaningsih, Hendriyana, Subagjo	223
CT.03	Preparation of a Hydrocracking Catalyst by Combining The Components of Zeolite Y from Kaolin, Amorphous Silica Alumina and NiMo Active Metals	Endang Sri Rahayu, Subagjo, Tjokorde Walmiki Samadhi, Melia Laniwati Gunawan	235
CT.04	Characterization and Activation of Cement Kiln Dust as Heterogeneous Catalyst for Biodiesel Transesterification Process	Wahyudin, Joelianingsih, Hiroshi Nabetani, Nanik Purwanti, and Armansyah H. Tambunan	245
CT.05	Measurement of SO ₂ Adsorption Capacity of CuO/ γ -Al ₂ O ₃ Prepared using Dry Impregnation	Yuono, David Bahrin, Subagjo and Herri Susanto	255

INDUSTRY

Code	Title	Authors	Page
IN.03	Experience Shared in Managing Cooling Water Treatment for 30 th Years Old Ammonia Plant	Rahayu Ginanjar Siwi, Iswahyudi Mertosono, Rahadiyan Dewangga	263



CHEMMPRO 2014

October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
in conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

MATERIAL PROCESSING

Code	Title	Authors	Page
MAP.01	Degradation of Chitosan to Make a Medically Standard of Oligochitosan	Noor Anis Kundari, Kartika Cahyani, Maria Christina Prihatiningsih, and Bangun Wasito	277
MAP.02	Hot Corrosion of Aluminide Coated Ti-Al-Cr-Nb-Zr-Y Intermetallic Alloys	Ahmad Fauzi, Djoko H. Prajitno, and Eddy Agus Basuki	291
MAP.03	Microstructural Evolution and Oxidation Behavior of Fe-Ni-Al Alloys at High Temperatures	Cholidah Akbar Fitriani and Eddy Agus Basuki	301
MAP.04	Prediction of Al ₂ O ₃ Ceramic Mechanical Structure by Adding Aditive and Sintering Temperature Processed by Neural Network	Moh Ilfan Jauhari, Zulkifli, Detak Yan Pratama	309
MAP.05	Corrosion Database Development	Muh Ashadi Cangara, Tjokorde Walmiki Samadhi, Isdiriyani Nurdin & Hary Devianto	321
MAP.06	The Effect of Tannin on Carbon Steel Corrosion in Nitric Acid Solutions	Anna Sonya Asoka, Listiani Artha, Isdiriyani Nurdin, and Hary Devianto	331

MINERAL PROCESSING

Code	Title	Authors	Page
MIP.01	The Study of Coal Ratio Effect on Smelting Processes of Carbonat Type of Copper Ore Using Mini Blast Furnace (MBF)	Pintowantoro, Sungging and Abdul, Fakhreza	343
MIP.02	Modelling and Simulation of Coal Gasification Using ASPEN PLUS	Daniel Prasetyo, Dwiwahju Sasongko, and Winny Wulandari	355
MIP.04	Process modelling of two-steps dimethyl ether synthesis from Berau coal by indirect coal liquefaction	Abdurrahman Fadhli Halim Luthan, Dwiwahju Sasongko, and Winny Wulandari	375
MIP.07	Separation of Cobalt and Nickel by Solvent Extraction using Cyanex 272 and Nickel Stripping Behavior under Variations of Temperature and Volume Ratio of Aqueous to Organic Solution	F. Syarifah, S. Purwadaria, M.Z. Mubarak	393



October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
 In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

Code	Title	Authors	Page
MIP.08	Treatment of Artificial Gold Preg- Robbing Ore by Blinding Agent and Its Synergistic Effect With Resin-in- Leach for Improving Gold and Silver Recoveries	M.Z. Mubarak and P.S. Irianto	407
MIP.09	Effects of Burner Rearrangement on Fuel Consumption in A Steel Stock Reheating Furnace	Irawan. A and Bindar. Y	423
MIP.10	Reduction of Nickel Laterite Ore from South East Sulawesi	Solihin	431
MIP.13	Coal Processing and Recycling Technology for Foundry Cokes and Carbon Raiser Production and Its Application for Metallic Mineral Reduction	Anggoro Tri Mursito, Dina Syazwani, Alia Najiah, Aditya Wibawa and Bagus Dinda Erlangga	437



CHEMPRO 2014

October 30th - 31st 2014, Bandung, Indonesia

CATALYST
CT.04

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

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

Wahyudin^{1,3}, 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



CHEMMPRO 2014

October 30th - 31st 2014, Bandung, Indonesia

CATALYST
CT.04

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

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.



October 30th - 31st 2014, Bandung, Indonesia

CATALYST
CT.04

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

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.



October 30th - 31st 2014, Bandung, Indonesia

CATALYST
CT.04

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

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 Tungal 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.

Tabel 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

Tabel 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.

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.

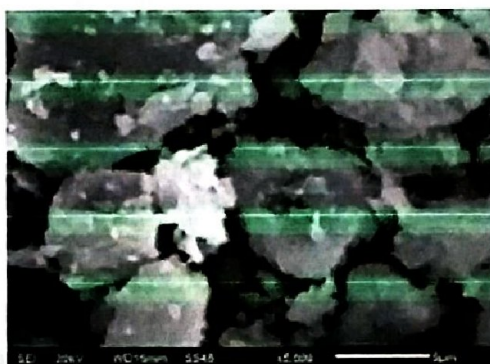


Figure 1 Fresh cement kiln dust (original)

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.

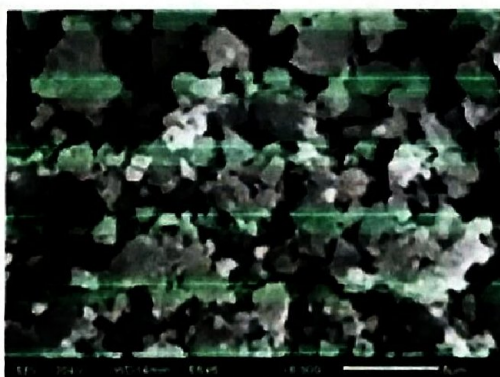


Figure 2 Activated cement kiln dust with methanol



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.

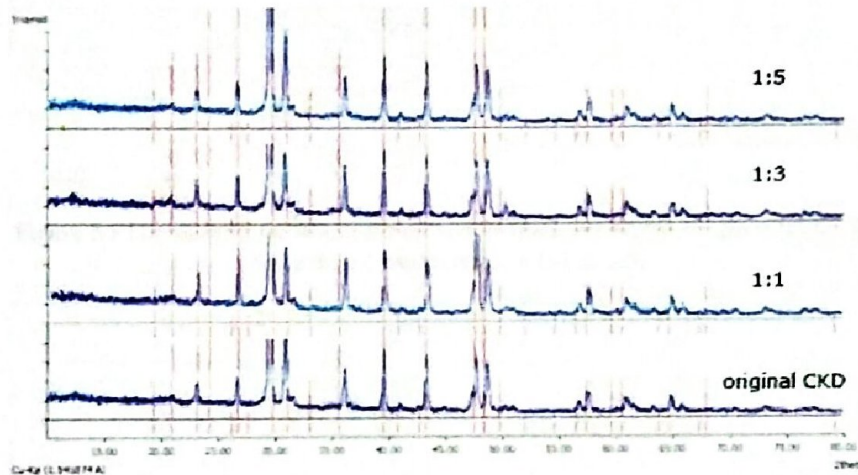


Figure 3 XRD analysis of activated cement kiln dust with various CKD to methanol weight ratio (1:1; 1:3; 1:5)

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.

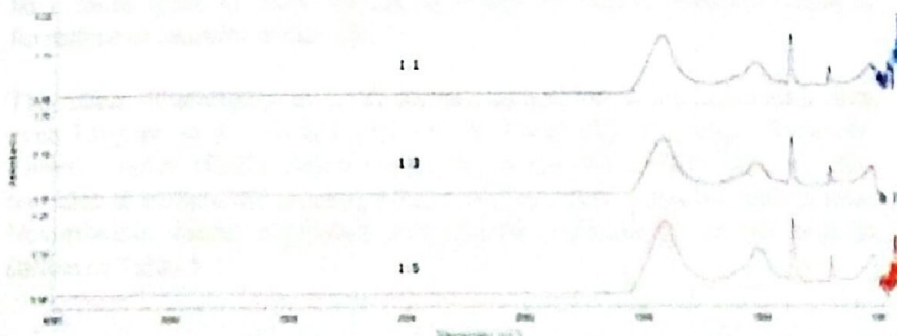


Figure 4 FTIR analysis for 15 minute activation of cement kiln dust with various CKD to methanol weight ratio (1:1; 1:3; 1:5)



CHEMMPRO 2014

October 30th - 31st 2014, Bandung, Indonesia

CATALYST
CT.04

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

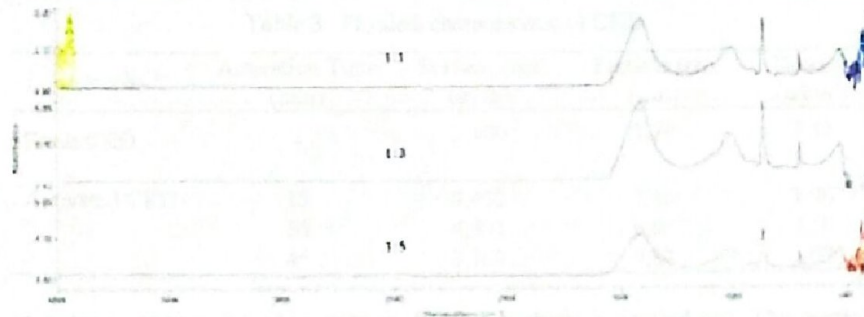


Figure 5 FTIR analysis for 30 minute activation of cement kiln dust with various CKD to methanol weight ratio (1:1; 1:3; 1:5)

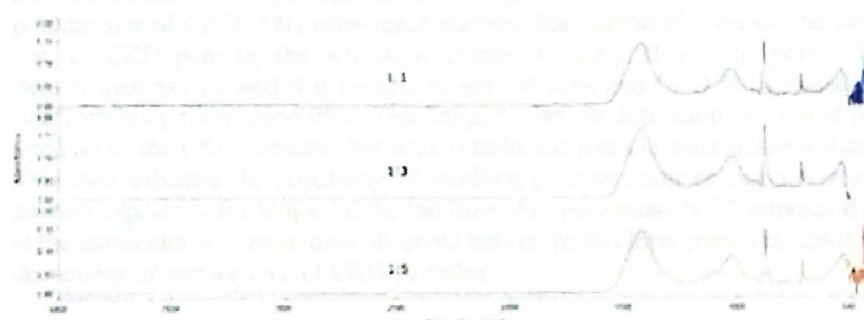


Figure 6 FTIR analysis for 45 minute activation of cement kiln dust with various CKD to methanol weight ratio (1:1; 1:3; 1:5)

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.



CHEMMPRO 2014

October 30th - 31st 2014, Bandung, Indonesia

CATALYST
CT.04

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

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.

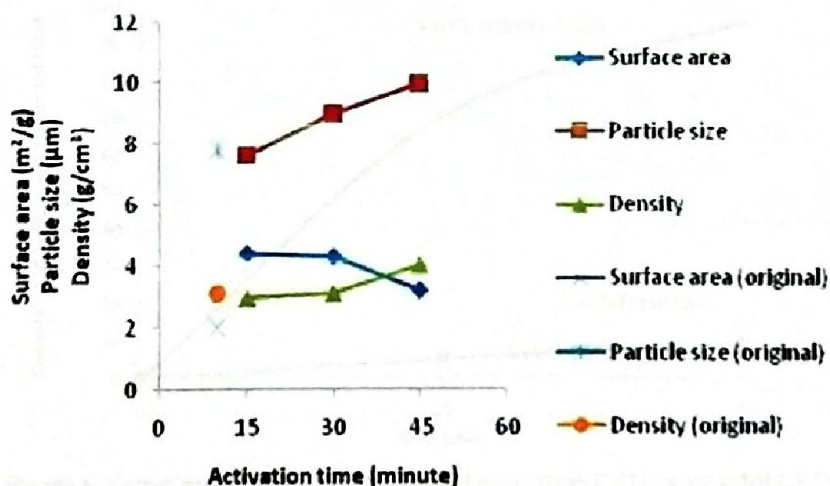


Figure 7 Analysis of activation time effect to CKD particles



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 ($^1\text{H-NMR}$) 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.

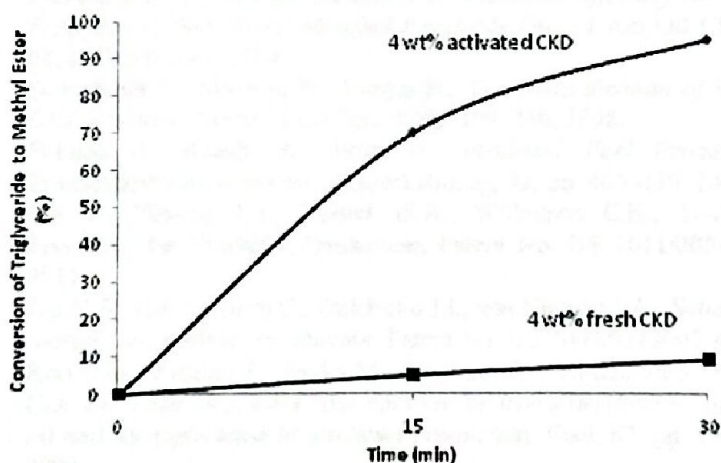


Figure 8 Conversion of triglyceride to methyl ester: fresh CKD vs activated CKD



October 30th - 31st 2014, Bandung, Indonesia

CATALYST
CT.04

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

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.

5 Acknowledgement

Part of this work is funded by Ministry of Research and Technology through grant program of Insentif Riset Sistem Inovasi Nasional (INSINAS) No. 27/SEK/INSINAS/PPK/I/2014. The authors gratefully acknowledge the help and support for this research by Erfin Y. Febrianto, Agung Nugroho and Lia Nirwana Sari.

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.