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## Transesterification of Waste Cooking Oil using Chemically Treated Catalyst

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**Abstract:** This study presents the potential of a chemically treated cement clinker as the catalyst for biodiesel production. Activation was achieved by means of chemical treatment with either KOH or CH<sub>3</sub>OH and in some case followed by calcination. The catalysts effects were studied under constant condition by using 1.5 wt.% of catalyst, 5:1 for methanol to oil ratio, at temperature of 60°C and the reaction time of 3 h. The feedstock was waste cooking oil obtained from a local household. Basic strengths and surface morphology of the catalyst were analyzed using Hammett indicators and SEM and their influences to the biodiesel conversion were elucidated. The FAME compositions were analyzed using GC-MS. It was found that the KOH impregnated catalyst without calcination give the highest conversion of FAME (96.8%). The catalyst with high basicity produces higher biodiesel conversion.

**Key words:** Transesterification, catalyst, cooking oil, biodiesel

### INTRODUCTION

Biodiesel or Fatty Acid Methyl Ester (FAME) is a renewable, biodegradable and alternative fuel for diesel engines obtained from transesterification of vegetable oils or animal fats with alcohols. Biodiesel production using edible oil is not currently feasible due to high feedstock cost; approximately 80% of the overall cost. Utilisation of lower cost vegetable oil such as Waste Cooking Oil (WCO) may be able to reduce the overall cost of biodiesel production (Noshadi *et al.*, 2012). Furthermore, utilization of waste cooking oil circumvents the oil vs. food issue which has become a hotly debated issue during past few years. The consumption of cooking oil is increasing and its consistent supply makes waste cooking oils as commercial viable feedstock. Approximately, there are about 3 billion liters of cooking oil consumed in Malaysia annually, for which about 30% of WCO available for biodiesel production translating to about 10% of diesel demand in Malaysia. WCO has a great potential to be main feedstock for biodiesel production and has shown to produce biodiesel compliant with international standard ASTM D6751 besides having a significant reduction in exhaust emission compared to petrodiesel (Kumaran *et al.*, 2011). However, converting WCO to biodiesel present greater challenges due to its high FFA value and water

content which may cause soap formation instead of biodiesel. For instance, FFA greater than 1 wt.% resulting in lower yield of biodiesel by causing soap production (Wan Omar and Amin, 2011; Azcan and Yilmaz, 2012).

Heterogeneous base catalysts have advantages of being reusable, noncorrosive, show greater tolerance to water and FFAs in feedstock, improve biodiesel yield and purity, have a simpler purification process for glycerol and are easy to separate from the biodiesel product (Ilgen and Akin, 2009; Jairam *et al.*, 2012; Xie *et al.*, 2006). Many type of heterogeneous catalyst were investigated for biodiesel production from vegetable oil such as alumina based (Ilgen and Akin, 2009), oyster shell (Jairam *et al.*, 2012) and calcined Mg-Al hydrotalcites (Xie *et al.*, 2006).

Calcium Oxide (CaO) is one of the most common used heterogeneous base catalysts for the transesterification of vegetable oil. Producing biodiesel using CaO as a solid base catalyst has many advantages, such as higher activity, mild reaction conditions, reusable and low cost (Liu *et al.*, 2008; Kawashima *et al.*, 2008; Hsiao *et al.*, 2011). Limestone which is a main source of CaO is available abundantly in Malaysia which is mainly used for cement manufacturing. Therefore, this study aims to prepare a cheaper catalyst from cement clinker that is easy to recover apart from providing an efficient conversion of vegetable oil to biodiesel. Cement clinker is an

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intermediate during production of cement. This work aims to study the influence of catalyst activation and treatment method to WCO transesterification.

### MATERIALS AND METHODS

**Catalyst preparation and characterization:** CC/KOH and CC/CH<sub>3</sub>OH were prepared by mixing 50 g of fresh cement clinker with 10 wt.% of aqueous potassium hydroxide and methanol, respectively. The impregnation process was subjected to a vigorous stirring for 24 h. The resultant slurry was filtered and the filter cake is dried at 373K. The dried catalysts were sieved to obtain the particles size at ≤71 μm. A portion of the catalysts was calcined at 773 K in a muffle furnace (Carbolite, CWF1200) for 5 h. Basic strength of the prepared catalysts was determined using Hammett indicators. About 50 mg of sample was shaken in 10 mL of methanol solution of indicator and left to equilibrium for 2 h. The color changes were observed. In these experiment, the Hammett indicator used are bromothymol blue (H = 6.8), phenolphthalein (H = 9.8), 2,4-dinitroaniline (H = 15) and 4-nitroaniline (H = 18.4). The scanning electron microscope (SEM, ZEISS EVO 50) was used to examine surface morphology for both fresh CC and activated CC catalyst.

**WCO transesterification:** Waste cooking oil was collected from a local household. The waste cooking oil is first filtered through a wire-mesh filter to remove food particles and other contaminants prior to analysis of their free fatty acid content. A 1 L two-necked glass flask with water-cooled condenser was used with 30 mL of waste cooking oil, 150 mL methanol (volume ratio oil: methanol of 1:5) and the CC catalyst loading of 1.5 wt.% (relative to total mass of reactants). The oil was first mixed in methanol directly in the flask until it reached reflux temperature at 60°C which the catalyst then added. The reaction was carried out at maximum stirring rate using a magnetic stirrer for three hours. The temperature inside the reaction flask is maintained at 60°C. Subsequently, the mixture was placed into a separating funnel and was kept at ambient air for several hours until three distinctive liquid layers appeared. The upper layer is biodiesel; the middle layer is glycerol and bottom layers are the catalyst as shown in Fig. 1. The methyl ester is separated from glycerol and catalyst using a centrifuge. The methyl esters layer obtained is washed three times using warm water of 50-55°C to remove methanol and glycerol before dried using sodium sulfate anhydrous to remove moisture content.

**Analytical methods:** Acid values were determined according to the methods prescribed by Zhu *et al.* (2011). Acid values were calculated using following formula:



Fig. 1: Three separated layers after transesterification of WCO

Table 1: Fatty acids composition in waste cooking oil

Properties	This work	Lam <i>et al.</i> (2010)
Fatty acid composition (%)		
Lauric (C12:0)		0.10
Myristic (C14:0)	0.80	1.0
Palmitic (C16:0)	32.88	42.8
Palmitoleic (16:1)	1.38	
Margaric (C17:0)	0.61	
Stearic (C18:0)	5.19	4.5
Oleic (C18:1)	38.45	40.5
Linoleic (C18:2)	10.01	10.1
Linolenic (C18:3)		0.20
Acid value (mg KOH/g)	1.24	

$$AV = \frac{V \times c \times 56.11}{m} \quad (1)$$

where, AV (mg KOH/g) represents the sample acid value; V (mL) is the volume of potassium hydroxide standard titrant solution consumed; c (mol/L) represents potassium hydroxide standard titrant solution concentration and m (g) is the weight of 1ml sample.

The WCO and FAME composition was determined using Gas Chromatography Mass Spectrometry (GCMS) according to ASTM D6584. The samples of oil and FAME from transesterification process were taken and dissolved in n-Hexane GC/HPLC grade prior to be injected into the GCMS for triglycerides analysis. Triglyceride analysis was performed using Agilent 7890A GC System equipped with Agilent 7683B Series Injector, 5975C Inert MSD and a DB-1 column with temperature range of 60-340°C. Fatty acids composition in WCO was determined as presented in Table 1 which shows the most abundant fatty acids in WCO were oleic, palmitic and linoleic acids.

**RESULTS AND DISCUSSION**

**Comparison of KOH and methanol treated catalysts:**

Comparison on CC catalyst activated with KOH and methanol is presented in Table 2 and Fig. 2. The preparation method of CC catalysts involved wet-impregnation and calcination method. After impregnation with KOH or methanol, the surface of CC catalyst will be coated with the layer of chemical solution and the basic strength is increased. The base strength of CC catalyst activated with different chemicals was measured using Hammett indicators. The calcination produces a catalyst with high basicity compared to the catalyst without calcination. Calcination also promotes porous surface formation on the surface of catalysts due to thermal decomposition or phase transition.

The SEM results of fresh CC and CC/KOH(b) samples showed the changes of surface morphology before and after activation. Evidently, as shown in Fig. 3b, the surface of catalyst develops into more porous and this

structure is important for the catalyst as they are associated with higher surface area and hence promotes better reaction.

**Composition of FAME:** Biodiesel obtained from the transesterification process using methanol as reactant is a mixture of long chain fatty acid methyl esters. Otherwise, if ethanol used as reactant the product is known as Fatty Acid Ethyl Esters (FAEE). Most of the previous work reported that methanol is favorable due to its availability and lower cost. Composition of Fatty Acid Methyl Esters (FAME) may vary according to both the catalyst and feedstock used (Lam *et al.*, 2010). In the present study, sodium methoxide ( $\text{CH}_3\text{ONa}$ ) was used as a standard

**Table 2: Different prepared catalysts**

Catalysts	Preparation method	Basic strength (H)
CC/KOH(a)	Impregnation and calcination	9.8<H<15
CC/KOH(b)	Impregnation	9.8<H<15
CC/CH <sub>3</sub> OH(a)	Impregnation and calcination	9.8<H<15
CC/CH <sub>3</sub> OH(b)	Impregnation	H≤9.8

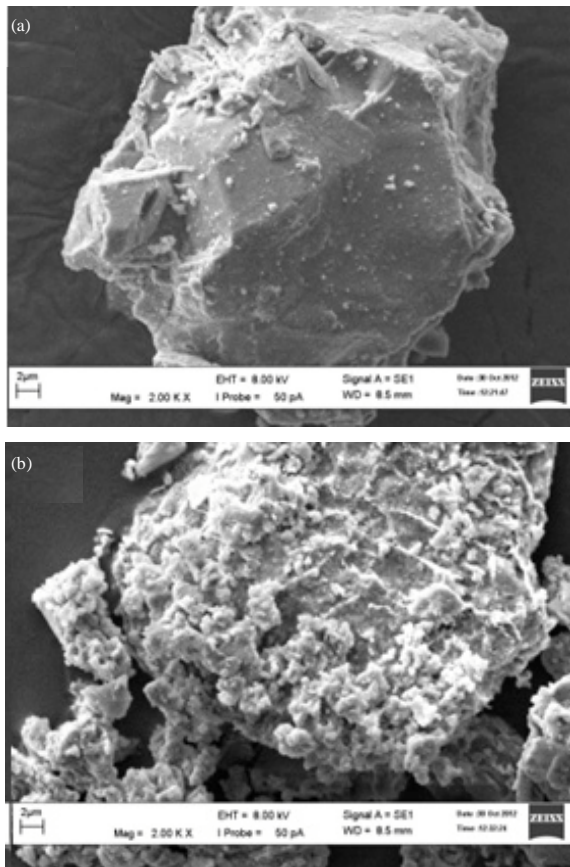


Fig. 2(a-b): SEM images of (a) Fresh CC and (b) CC/KOH(b) catalysts

Table 3: Fatty acid methyl esters composition from transesterification of WCO

FAME content (%)	Type of catalyst				
	CC/KOH(a)	CC/KOH(b)	CC/CH <sub>3</sub> OH(a)	CC/CH <sub>3</sub> OH(b)	CH <sub>3</sub> ONa
Methyl myristate					2.18
Methyl palmitate	40.15	36.32	27.72	35.35	38.71
Methyl palmitoleate	2.19				1.23
Methyl stearate	4.42	5.79	4.52	5.4	5.44
Methyl linoleate	9.15	5.72	8.87	9.63	
Methyl ricinoleate	1.45		18.35		
Methyl elaidate	34.67	44.06	30.42	36.93	48.36

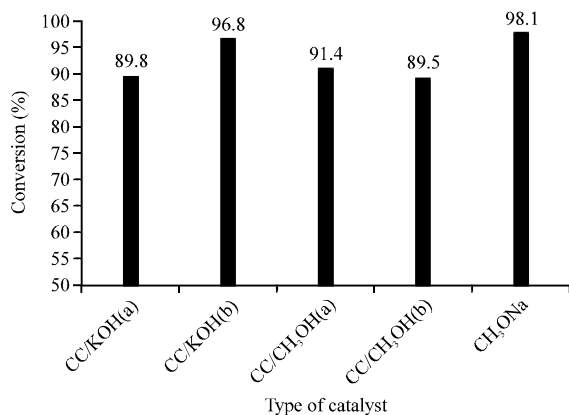


Fig. 3: Effect of chemically treated catalysts on WCO conversion

catalyst. As shown in Table 3, the highest FAME contents in product were methyl elaidate and methyl palmitate which account for over 70% of the FAME. Only a small variation of methyl ester composition was observed because a similar feedstock (WCO) was used throughout this study.

**Conversion of FAME:** Catalyst activation may affect the WCO transesterification conversion and yield. Figure 3 shows the influence of catalyst activation on conversion of WCO to FAME. The results suggest that WCO transesterification achieved higher conversion using KOH treated catalyst. KOH have been used commercially in biodiesel industries as homogeneous catalyst for some time. This work uses KOH to chemically treat cement clinker resulting in increased basic strength for the heterogeneous catalyst and hence achieving higher conversion to FAME. Calcination may induce thermal decomposition releasing CO<sub>2</sub> and freeing alkali metal compounds such potassium, which may improve the catalytic activity. Among the catalysts used, CC/KOH(b) which without calcination exhibit a comparatively high conversion of 96.8% and comparable to standard catalyst, sodium methoxide with conversion of 98.1%. While for CC/CH<sub>3</sub>OH(a), the conversion is about 91.4% which is higher than CC/KOH(a) catalyst. This may be because of CC/CH<sub>3</sub>OH(a) catalyst that impregnated

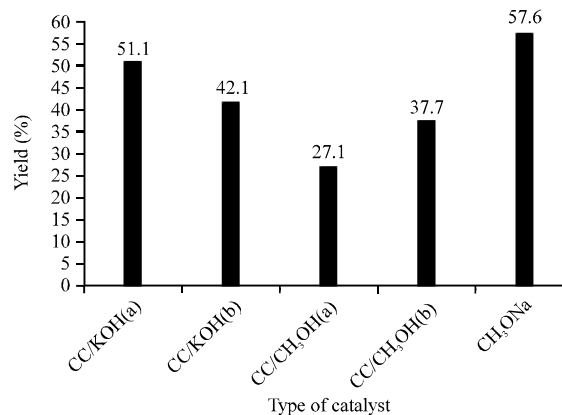


Fig. 4: Effect of chemically treated catalysts on biodiesel yield

with methanol and was calcined. The calcination process could produce methoxide resulting in higher conversion.

**Yield of FAME:** Figure 4 shows the yield of FAME using various catalysts. Generally the yield of FAME in this work for catalysts CC/KOH(b), CC/CH<sub>3</sub>OH(a) and CC/CH<sub>3</sub>OH(b) are below 50%. Besides, FAME yield using CH<sub>3</sub>ONa as the standard catalyst, only produces about 57.6% compared to previous study by Azcan and Yilmaz (2012) which is over 76%. Although CC/KOH(b) produces higher conversion than the CC/KOH(a) as shown in Fig. 3, the FAME yield is actually much lower at 42.1%. This suggests a higher formation of byproduct such as glycerin and soap. CC/KOH(a) gave high yield of FAME of 51.1% almost comparable to that of CH<sub>3</sub>ONa. The yield of FAME may be influenced by the transesterification process as in this study. For instance, the fixed amount of catalyst loading employed throughout this work could not increase the FAME yield. Moreover, longer reaction time favour formation of glycerin and soap causing the reduction of FAME yields.

## CONCLUSION

Chemically activated limestone based catalyst shows a good potential as an alternate for one-step transesterification of low FFA waste cooking oil.

Activation using KOH was found to give the highest WCO conversion to FAME at 96.8% and FAME yield of 51.1%. The results suggest that the catalyst employed in this work might be useful as a new low cost catalyst for biodiesel production.

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#### REFERENCES

- Azcan, N. and O. Yilmaz, 2012. Microwave assisted transesterification of waste frying oil and concentrate methyl ester content of biodiesel by molecular distillation. *Fuel*, 104: 614-619.
- Hsiao, M.C., C.C. Lin and Y.H. Chang, 2011. Microwave irradiation-assisted transesterification of soybean oil to biodiesel catalyzed by nanopowder calcium oxide. *Fuel*, 90: 1963-1967.
- Ilgen, O. and A.N. Akin, 2009. Development of alumina supported alkaline catalysts used for biodiesel production. *Turk. J. Chem.*, 33: 281-287.
- Jairam, S., P. Kolar, R. Sharma-Shivappa, J.A. Osborne and J.P. Davis, 2012. KI-impregnated oyster shell as a solid catalyst for soybean oil transesterification. *Bioresour. Technol.*, 104: 329-335.
- Kawashima, A., K. Matsubara and K. Honda, 2008. Development of heterogeneous base catalysts for biodiesel production. *Bioresour. Technol.*, 99: 3439-3443.
- Kumaran, P., N. Mazlini, I. Hussein, M. Nazrain and M. Khairul, 2011. Technical feasibility studies for Langkawi WCO (waste cooking oil) derived-biodiesel. *Energy*, 36: 1386-1393.
- Lam, M.K., K.T. Lee and A.R. Mohamed, 2010. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. *Biotechnol. Adv.*, 28: 500-518.
- Liu, X., H. He, Y. Wang, S. Zhu and X. Piao, 2008. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel*, 87: 216-221.
- Noshadi, I., N.A.S. Amin and R.S. Parnas, 2012. Continuous production of biodiesel from waste cooking oil in a reactive distillation column catalyzed by solid heteropolyacid: Optimization using response surface methodology. *Fuel*, 94: 156-164.
- Wan Omar, W.N.N. and N.A.S. Amin, 2011. Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology. *Biomass Bioen.*, 35: 1329-1338.
- Xie, W., H. Peng and L. Chen, 2006. Calcined Mg-Al hydrotalcites as solid base catalyst for methanolysis of soybean oil. *J. Mol. Cat. A: chem.*, 246: 24-32.
- Zhu, Y., J. Xu and P.E. Mortimer, 2011. The influence of seed and oil storage on the acid levels of rubber seed oil, derived from *Hevea brasiliensis* grown in Xishuangbanna, China. *Energy*, 36: 5403-5408.