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Contributed Paper

# Biodiesel Synthesis from Transesterification by Clay-based Catalyst

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## ABSTRACT

Transesterified biodiesel produced by clay-based catalyst had been mainly investigated with the characterization of fuel properties. The catalysts were prepared by impregnation between aqueous solution and Suratthanee black (SB) clay and Ranong kaolin (RK) with a controlling catalyst. All biodiesel products were characterized by gas chromatography, viscosity, flash point, cloud point, pour point and carbon residue consecutively. The major component of the obtained biodiesels was identified to be methyl palmitate. Based on short time of reaction, it was found that the calcium oxide impregnated on Ranong kaolin has better catalysis performance over that of Suratthanee black clay. Compared to various properties of biodiesel, it provided higher viscosities and higher carbon residue than those of high speed diesel fuel. It can be concluded that these biodiesels from clay–based catalysts have some encouraging properties to supersede low speed diesel fuel and to lower the cost of production in some extent.

**Keywords**: biodiesel, clay-based catalysts, renewable fuel, transesterification.

## 1. INTRODUCTION

From the crisis of oil price eruption and increasing demand of oil, they both activated industrial chemists and chemical engineers to find an alternative fuel worldwide. One of them has been emphasized on biodiesel production from transesterification of waste vegetable oil[1,2] ,sunflower oil [3] and soy bean oil[4]. Then, we address the biodiesel production by clay-based catalyst and investigate in some extent.

With organic chemistry, transesterification is written in Fig. 1. It tells us that glycerin will come out as co-product every time. Taking some advantages, Thailand supplies a great number of various vegetable oil and it should produce biodiesel from agriculture products to increase energy security domestically. Another point of natural clay in Thailand, it is available throughout the country. So clay-based catalyst should be prepared and applied for this biodiesel process. After literature survey, some researchers worldwide have investigated clay catalysts for esterification and transesterification but not for biodiesel production. Firstly, Prakash [5] et al. reported transesterifcation of dicarboxylic acid with various alcohols by Mn$^+$-montmorillonite clay catalysts and then, his group [6] had continuously used Indian bentonite as esterification catalyst for ester synthesis. While, Duboius et al.[7] had prepared biodegradable polyester by transesterification catalysts to improve clay exfoliation. Finally, Liu [8] produced ethyl/methyl $\beta$-ketoester by montmorillonite K-10 as an efficient reusable catalyst. This is the reason why we have selected the natural clay as a basic component of transesterification catalyst to produce biodiesel. And there has been no clear reports telling about the transesterification for biodiesel by clay-based catalyst. This short communication will be worth reporting biodiesel production by catalyst from clay sources in Ranong province and Suratthanee province from domestic resource.

The obtained biodiesels were also characterized some fuel properties, for examples, viscosity, flash point, pour point, cloud point and Conradson carbon residue. These will support that the biodiesel from clay-based catalyst will be another encouraging method for fuel production. The objective for this research is divided into three main points. There are the synthesis of clay-based catalyst and the transesterification of palm oil to biodiesel and characterization of biodiesel compared to petroleum diesel. After characterization, some important properties of biodiesel were compared to that of diesel standard regulated from Thailand's authorities. This short communication is not emphasized on clay-based catalyst characterization but mainly reports the obtained biodiesel properties in comparison with petroleum diesel.

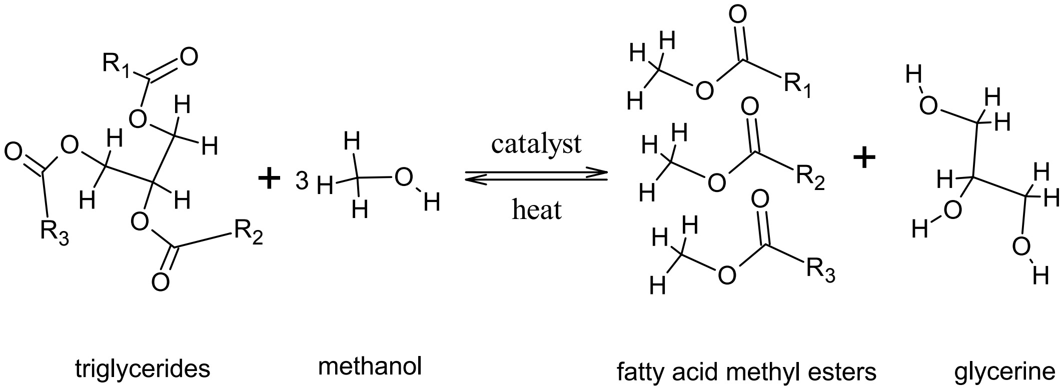

**Figure 1.** Transesterification reaction of triglyceride to FAME (fatty acid methyl ester).

## 2. MATERIALS AND METHODS

### 2.1 Chemicals Used and Apparatus

Suratthanee black clay (SB) was taken from Nasarn district in Suratthanee province in the same way as Ranong kaolin (RK) was from Muang district, Ranong province. Both clay are in powder and used as it was supplied. Methanol with commercial grade, it was supplied by A.T. Sci. Trading Co. It would be used without purification. Refined palm oil manufactured in June 2005 was Morakot cooking oil which was frequently available in grocery stores and was the reactant in this experiment. The compositions of refined palm oil were 32-47 % wt of palmitic acid and 40-52% wt of oleic acid and trivial amount of diglycerides and moisture less than 1 % wt. For n-hexane, sodium hydroxide, calcium oxide, aluminium oxide in spherical shape, they were all from Fluka Co., with AR grade the purities of nearly 99%.

Biodiesel product was determined by gas chromatography (Hewlett Packard, HP 6890) with FID detector in the off-line mode. The GC column capillary was 10 m long with the diameter of 100 $\mu$m. Using He gas in GC, it became the carrier gas and hexane as solvent for biodiesel product. The oven temperature of GC was 150 $^0$C initially and 250 $^0$C as detection temperature.

### 2.2 The preparation method of catalyst

Two types of clay catalysts were prepared for transesterification between palm oil and methanol. They were the natural catalyst as a major component in the catalyst formulation -Suratthanee black clay (SB) and Ranong kaolin (RK). They were impregnated catalysts. The weight ratio between calcium oxide and each clays varied from 5:5, 6:4 and 7:3, respectively. After impregnation, the obtained catalyst precursor would be dried at 150 $^0$C, 30 min and, then, calcination at 950 $^0$C for 3 hr under ambient condition. Another catalyst was prepared by calcium sulfate impregnation on aluminum oxide (CAl) as a controlling catalyst. It also followed the same procedures of drying and calcinations as the previous type. Aqueous solution of NaOH was also used to transesterification in the same system and it produced biodiesel product called Bio-NaOH for its short name.

### 2.3 Catalyst testing of transesterification

Each run, 100 g of methanol and 10 g of calcined catalyst were firstly mixed and refluxed at 80 $^0$C for 1 hr as the catalyst activation step. The ratio of methanol: palm oil is kept constant of 2:5 without any changes in this research. Secondly, the 250 g of refined palm oil had been added to transesterify for 8 hr. The weight ratio among methanol: catalyst: palm oil was 10: 1 : 25. During the reaction, every 2 hr., the mixture in the reaction was successively taken and characterized. The schematic diagram of experimental set up was illustrated in Fig. 2. All sampling solutions were filtered to remove catalyst particle and impurities prior to biodiesel analysis. Then they became clear and ready for further determination of biodiesel properties after glycerol/ biodiesel separation. The clay-based catalyst was not reused since it was cheap and easily prepared in comparison with the other catalyst.

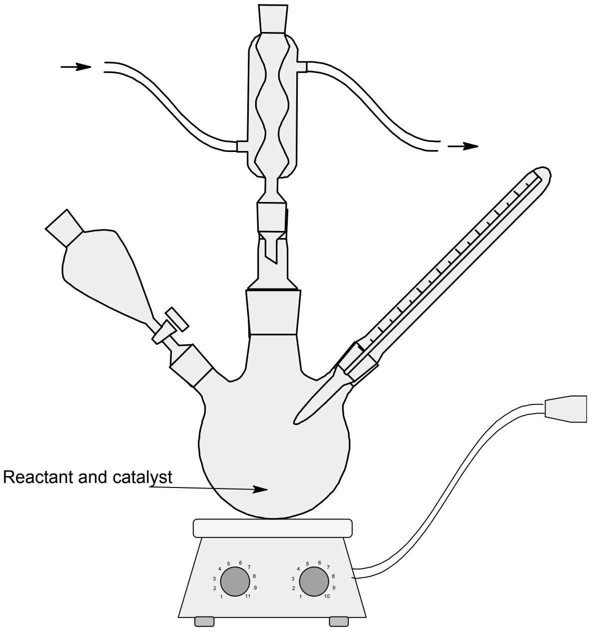

**Figure. 2.** Experimental setup for transesterification of palm oil.

### 2.4 Determination of Biodiesel Properties

For the fuel properties, the 5 major methods were characterized for all products of biodiesel. They consisted of Saybolt kinematic viscosity (ASTM D2161-87) at 37.8 $^0$C and 100 $^0$C, flash point (ASTM D93-90), cloud point (ASTM D2500-91), pour point (ASTM D97-87), and Conradson carbon residue (ASTM D189-88).

Saybolt viscometer is supplied by Koehler Instrument Co., modeled K 21420. The closed-cup apparatus for flash point determination is model K 16270 from Koehler Instrument Co. as well. According to minimized error and contamination across the different method, we use the new and separated samples carefully. But this short communication did not report the testing by diesel engine as reported by Gimenez et al. [9] because of the unavailability of diesel testing machine.

## 3. RESULTS AND DISCUSSION

Within 8 hr of reaction period, the biodiesel products from palm oil were 90-95% purity. The condition is applicable for small-manufacturing entrepreneur but not for very large scale as petrochemical industries. The co-products were glycerol and hydrolyzed diglyceride and moisture less than 10% wt in total. While the excess amount of methanol is minimized from the catalyst calculation prior to the reaction. Another post-treatment for the residue methanol, it was removed by 110$^0$C boiling for 3 hr. after biodiesel separation. The basic requirements of biodiesel separation were catalyst filtration and glycerol separation, then biodiesel products were without methanol and moisture. Additionally, the reaction time spent 8 hr, it would be assumed that all of the triglycerides were entirely consumed. In Fig. 3, biodiesel products from all types of catalysts were determined by GC analysis. The product identification was assigned as methyl palmitate or methyl ester as reported in Conceicao et al. [10]. It meant that CAl catalyst could not produce biodiesel. But the biodiesels from clay-based catalysts gave GC peak at the same position as that of methyl palmitate at 10 min. of peak position. Another peak at 11 min was speculated to be methyl oleate because C$_{18}$ in oleic acid. It showed a slightly higher in retention time. The evidence clearly indicated that RK catalyst

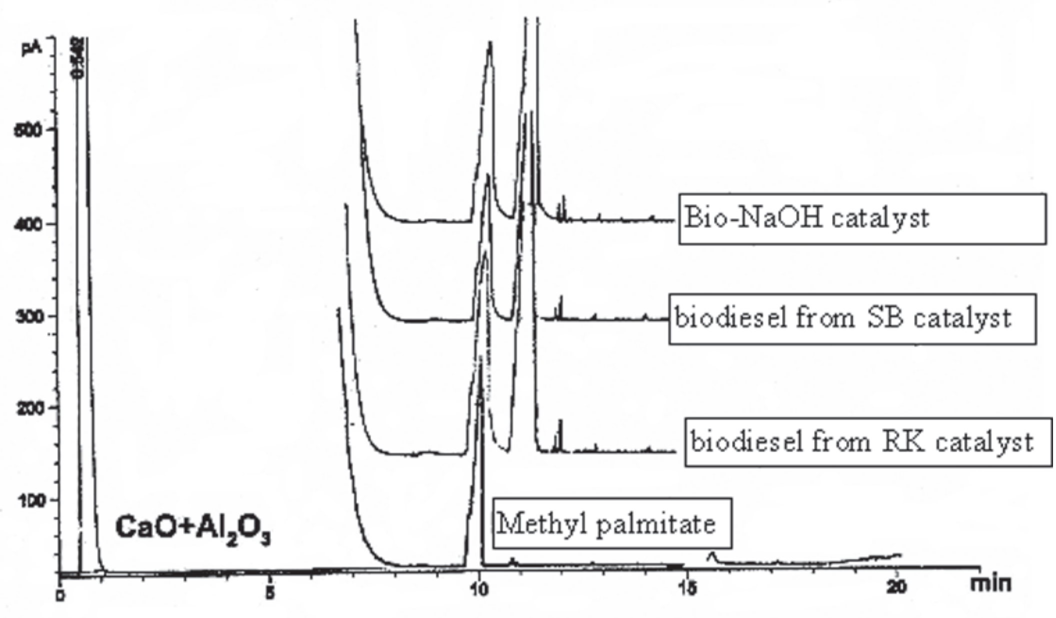

**Figure 3.** Gas chromatograms of biodiesel products derived from various catalysts.

produced biodiesel product better than SB catalyst at the initial period of reaction or clay-based catalyst applicable for biodiesel production in Figure 3.

In Table 1, the characterization of biodiesel properties was listed. All of biodiesel properties were different from refined palm oil. It showed that clay-based catalyst in this experiment produced biodiesel or transesterified products. Focusing on Saybolt kinematic viscosities at 37.8 $^{0}$C and 100 $^{0}$C, it was found that both SB and RK catalysts produced biodiesels with higher viscosities than petroleum diesel viscosity. Additional supportive reason is $C_8$-$C_{12}$ hydrocarbon component in petroleum diesel which differs from methyl ester of long chain fatty acid in biodiesel. It may be relevant to the presence of long chain of fatty acid ($C_{16}$-$C_{18}$) in triglyceride reactant [11]. But the viscosities of biodiesel are compromising properties to use in the range of low speed diesel fuel.

**Table 1.** Fuel properties of various biodiesels from transesterification system.

| Title | Palm oil | Bio-NaOH | SB | RK | Petroleum diesel | Diesel standards* | |
|---|---|---|---|---|---|---|---|
| | | | | | | Fast speed | Low speed |
| Viscosity at 37.8 $^{0}$C (cSt) | 45.1 | 5.29 | 4.97 | 5.41 | 3.32 | 8.0 | 1.8-5.0 |
| Viscosity at 100 $^{0}$C (cSt) | 7.88 | 0.95 | 1.2 | 1.36 | 0.36 | - | - |
| Flash point($^{0}$C) | 228.7 | 136.7 | 159.3 | 171.3 | 76.7 | 52 | 52 |
| Cloud point($^{0}$C) | 15 | 18 | 22.7 | 21.3 | 12.7 | - | - |
| Pour point($^{0}$C) | 7 | 9.7 | 12.7 | 12.3 | -0.7 | 16 | 10 |
| Carbon residue(%) | 4.96 | 1.63 | 0.56 | 0.12 | 0.32 | - | 0.05 |

**Note** Diesel standards from Thailand committee of Fuel specification

For flash point determination, SB clay catalyst gave 82.6 $^{0}$C but RK clay catalyst 94.6 $^{0}$C higher than 76.7$^{0}$C of petroleum diesel. Because the lower vaporizing fraction in obtained biodiesels was the contribution to higher flash point in this case. Comparison between Bio-NaOH catalyst and biodiesels from SB and RK clay-based catalyst, they gave higher flash points at 22-35 $^{0}$C. It revealed that NaOH catalyst gave biodiesel with lower flash point than that from Ca clay-based catalyst. Then clay-based catalysts produced biodiesel with higher flash points than petroleum diesel. Due to the presence of lower component with low flammable, it made the obtained biodiesels difficult to ignite in the internal combustion engine. But the higher flash point also suggested that the biodiesel would possibly be stored and handled more safety than petroleum diesel.

Another two properties had to be considered as cloud point and pour point. Cloud points of biodiesel from CaSB clay catalyst and CaRK clay catalysts, they have higher cloud point temperature than that of petroleum diesel of 10.0 $^0$C and 8.6 $^0$C, respectively. These differences are in the range of low speed diesel specification. After pour point determination, the biodiesels from CaSB and CaRK clay catalysts, they exhibited higher pour points than that from petroleum diesel. This is the contribution from the component of long chains in biodiesels especially methyl palmitate and possible methyl oleate. At that temperature, they form wax-like crystallization, on the other hand, it did not occur in petroleum diesel. The last one, Conradson carbon residue, both biodiesel gave 0.2 % slightly higher carbon residue than that of diesel. This is also the result of biodiesel composition and its combustion mechanism.

From the above result, clay-based catalysts from this studies produced biodiesel which had some potential to replace high speed diesel in the near future. But these clay-based catalysts will be characterized their surface acidity and area in the near future to reveal the correlation between the catalyst properties and biodiesel products.

## 4. CONCLUSION

From various characterizations of the obtained biodiesels, it can be concluded that CaSB and CaRK clay–based catalyst produced biodiesel products with higher viscosity and higher carbon residue than petroleum diesel. They possibly replace high speed diesel. Contrary to low speed diesel, the transesterification biodiesels provided compromising properties of Saybolt kinematic viscosities, pour point and Conradson carbon residue. So as to improve some properties, the further research is focused on lowering kinematic viscosity, flash point, pour point to upgrading the biodiesels close to petroleum diesel. The catalyst characterization will be examined extensively.

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