Biodiesel production from used palm oil using magnetic solid base catalyst

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Abstract. In this research the biodiesel from palm oil were synthesized by using magnetic solid base catalyst. The magnetic solid base catalyst was prepared by using co-precipitation method and followed by modified Stober’s method and wet impregnation method. CaO-ferrite nanometre magnetic solid base catalysts (CaO@Fe₃O₄/SiO₂) were synthesized by loading CaO on the surface of Fe₃O₄ core-shell using the polymeric binder, TEOS. Under the optimized condition reactions, the catalysts were synthesized by co-precipitation and incipient wetness impregnation followed by calcination at 700 °C for 5 h. The calcined catalyst was fully characterized. The basic strength of the catalysts (Hₑ) was first assessed using Hammett indicators, which are in range 9.8–15.0. The calcined Ca/ferrite-TEOS showed homogenous spherical shape with an apparent thickness of 92 nm. The FT-IR of CaO observed at 520 cm⁻¹ is attributed to the Ca-O vibrations. The EDX analysis confirmed the presence of Fe, Si and Ca on the catalyst. The optimization conditions for biodiesel production have been measured. The catalyst was used 5.0 % wt. The methanol to oil ratio is 5:1, reaction time is 180 minutes and reaction was produced at 80°C. The catalyst achieved a biodiesel conversion of used palm oil (acid value 1.2) above 92 %. The catalytic activity and recovery rate of CaO@Fe₃O₄/SiO₂ are better as compared to CaO catalyst. The properties of synthesized biodiesel have been studied and meet standard the Department of Energy Business.

Keywords: Biodiesel, Transesterification, Nanometer magnetic solid base

1. Introduction

Energy is a property of the sustainability of life and development of new technology or industrial processes. Energy consumption is steadily increasing on a global scale, while resources are decreasing especially petroleum [1]. With current rules of consumption, oil will be scarce in the next 50 years. Alternative energy resources such as biodiesel are therefore are attractive represent due to its clean, non-pollutant, non-toxic, degradable and environmental friendly properties. Biodiesels can be produced by using the transesterification process between fat or oil with alcohol such as methanol or ethanol [2, 3]. The reaction produces Fatty Acid Methyl Ester (FAME) as a main product with trace amounts of glycerol. Nowadays, the biodiesel production processes focus on the heterogeneous catalyst. It’s widely used because there are environmentally safe, easy to separate after reaction complete, and it can be reusable (with high yield) for many times, very least amount of waste water produced during the process and separation of biodiesel from glycerol is much easier [4-5]. However
the heterogeneous catalyst still had the some problems such as losing their catalytic surface and it is difficult to separate the catalyst from biodiesel after used for many cycle. [6-8]

In this work focus on developed heterogeneous catalysts by used magnetic catalyst to improve the separation method after the reaction complete.

2. Materials and Methods

2.1 Materials

The Palm oil (Commercially edible grade, Thailand) was obtained in the local supermarket. Methanol was analytical reagent (AR grade) from Merck Limited, Iron (III) chloride hexahydrate (AR grade) and Iron (II) chloride tetrahydrate (Ar grade) from Quality Reagent Chemical (QreC) and pure nitrogen gas from Linde (Thailand) limited.

2.2 Preparation of Magnetic core (Fe₃O₄)

Weigh 2.7 g of FeCl₃.6H₂O and 1g of FeCl₂.4H₂O (mole of Fe (II): Fe (III) = 1:2) and dissolve it with 50 ml of DI water (mix under N₂ atmosphere). Transfer the mix solution to 3-neck round bottom flask (250 ml). The resultant solution was left to be stirred for until the solution temperature higher than 80 °C (temperature of oil bath > 96°C (Stir under N₂ atmosphere). Then slowly add Conc. ammoniac (NH₃, 28%) to mixture solution with vigorous stirring to make a black solid product when reaction media reaches pH =10, then the resultant solution was left to be stirred for 1 h in 70 °C. After that remove the black magnetite solid product from the solution by used the magnetic and washed with 50 ml of DI water for 5 times follow by 50 ml of ethanol 2 times and then was dried at 60 °C for 6 h.

2.3 Preparation of Magnetic core with TEOS ( Fe₃O₄@SiO₂)

The Fe₃O₄@SiO₂ was prepared by a modified Stober method. Fe₃O₄ 0.5 g was dispersed in the mixture of ethanol (80 ml), deionized water (20ml) in 250 ml 3-neck round bottom flask) and ultra-sonication for 30 min. Next stir the mixture by used overhead stirrer and flow N₂ gas to the mixture. Followed by the addition of 2 ml of NH₃ (28%) and 2 ml of TEOS (add 250 μl of NH₃ follow by 250 μl of TEOSand stir for 5 min and add 250 μl of NH₃ follow by 250 μl of TEOS again). This solution was stirred mechanically for 4 h at room temperature. Then the Fe₃O₄@SiO₂, was separated by an external magnet, and was washed with 100 ml deionized water three times and 50 ml Ethanol 1 time, after that dried at 60 °C for 10 h. Finally the Fe₃O₄@SiO₂ was calcined at 500 °C for 2 h.

2.4 Preparation of Ca/(Fe₃O₄@SiO₂)

The Ca/(Fe₃O₄@SiO₂) was prepared by wetness impregnation method. First, weight Fe₃O₄@SiO₂ about 0.5 to g in three necks round bottom flask. Next, weight Ca(NO₃)₂ and dissolved in Di water by control the percentage of Ca²⁺ ion for 5%wt of Fe₃O₄@SiO₂ . After Stirred the mixture and flow N₂ gas for 3 h followed by heat until the solution was dried. Finally, the magnetic was dried at 100 °C for 10 h and calcined at 800 °C for 3 h and kept it in desiccators for the future used.

2.5 Catalyst characterization

The characterization of magnetic core, magnetic core with TEOS and magnetic catalyst were confirmed by a X-ray diffraction (XRD) using a Bruker AXS D8 Advance; Cu Kα1 radiation, λ=1.5406 Å measured from 20° to 80° (2θ) with a step size of 0.02°. SEM-EDX was performed on a JEOL, JSM-6390. BET surface area was determined by used model:3 flex, micromritics, USA. The basic strength of all samples were analyzed qualitatively using Hammett indicators such as methyl red.
(H_ = 4.2), bromothymol blue (H_ = 7.2), phenolphthalein (H_ = 9.3), 2,4-dinitroaniline (H_ = 15.0), 4-nitroaniline (H_ = 18.4).

2.6 Transesterification Reaction

The transesterification reaction from palm oil (acid value 1.2 mgKOH/g oil) and methanol for synthesis of biodiesel was prepared with two different method (under static and stirring conditions) and carried out in a two round-bottomed flask equipped with a cooled water condenser and hot plate. The reactions were carried out with the reaction condition was methanol to oil molar ratio 9:1, catalyst concentration 5% wt and reaction time 3 h with reaction temperature of 100 °C and 60°C for the reactions under static and stirring conditions, respectively. After the reaction, the catalyst was separated from the biodiesel by used outer magnetic. Then, excessive amount of methanol was removed by rotary evaporator.

3. Results and Discussion

3.1 Preparation of Magnetic core (Fe_3O_4) and Magnetic core with TEOS (Fe_3O_4@SiO_2)

The magnetic core (ferrite) was first synthesized under nitrogen atmospherere. The results show fine particle with agglomeration as presented in Figure 1.[9-10] The calcium oxide ferrite (CaO@Fe_3O_4/SiO_2) or Ca/FERRITE-TEOS was successfully synthesized by co-precipitation and incipient wetness impregnation followed by calcination. The TEOS cause the ferrite to combine and form shape, however the surface of sample show rough surface the EDS confirm the present of silicon from TEOS as shown in Figure 3 and Table 1.

![Figure 1](image1.png)

**Figure 1.** TEM (a and b) and SEM (c) of Magnetic core (ferrite).

![Figure 2](image2.png)

**Figure 2.** TEM (a and b) and SEM (c) of Magnetic + TEOS (ferrite-TEOS)
Figure 3. The EDS of Magnetic core (ferrite) (a) and Magnetic + TEOS (ferrite-TEOS) (b) and the IR spectrum of Magnetic + TEOS + CaO Calcined 700°C 5 h (Ca/ferrite-TEOS) (c).

Table 1 SEM-EDS of Magnetic core (ferrite) and Magnetic + TEOS (ferrite-TEOS)

| sample                  | Mass (%) |
|-------------------------|----------|
|                         | Fe       | O   | Si  | Ca |
| Ferrite                 | 81.93    | 18.07 | -   | -  |
| Ferrite-TEOS            | 69.53    | 21.18 | 9.30 | -  |
| Ca/ferrite-TEOS         | 52.56    | 28.79 | 12.12 | 6.53 |

The particle size of Ca/(Fe₃O₄@SiO₂) catalyst samples were in range of 50-70 nm and after calcination the catalyst show calcium oxide coated on surface with the particle size 15 nm. The higher percentage of Ca ion in magnetic catalyst may be from the uneven distribution during the process of preparing of catalyst. The calcined Ca/FERRITE-TEOS shows ferrite core with CaO coated on surface, which was confirmed by EDS (Table 1) and FTIR (Figure 3).

Figure 4. TEM (a and b) and SEM (c) of Magnetic + TEOS + CaO Calcined 700°C 5 h (Ca/ferrite-TEOS)

The basic strength of magnetic core, magnetic core with TEOS and magnetic catalyst were shown in were showed in Table 2. The basic strength of the catalysts (Hₐ) was first estimated using Hammett indicators method. The following Hammett indicators were used: methyl red (Hₐ=4.2), bromothymol blue (Hₐ= 7.2), phenolphthalein (Hₐ = 9.3), 2,4-dinitroaniline (Hₐ = 15.0), and 4-nitroaniline (Hₐ = 18.4). The results showed all of catalysts failed to convert 4-nitroaniline (Hₐ = 18.4) from yellow to orange and 2,4-dinitroaniline from yellow to red but all of catalyst could change the color of the bromothymol blue (Hₐ=7.2) from yellow to blue while only magnetic catalyst could
change the color of phenolphthalein ($H_\text{C}$ = 9.8) from colorless to purple. So the basic strength of magnetic core and magnetic core with TEOS could be approximately denoted as $4.2 < H_\text{C} < 7.2$ while magnetic catalyst could be approximately denoted as $7.2 < H_\text{C} < 9.8$.

**Table 2** Basic strength and biodiesel conversion of CaO and Ca/ferrite-TEOS catalyst

| sample                  | Basic strength | Conversion (%) | comments                      |
|-------------------------|----------------|----------------|-------------------------------|
| CaO                     | $9.8 < H_\text{C} < 15$ | 98.33          | Difficult to separate         |
| Ca/Ferrite-TEOS         | $9.8 < H_\text{C} < 15$ | 74.67          | Found some CaO in oil         |
| Ca/ferrite-TEOS calcined| $9.8 < H_\text{C} < 15$ | 96.01          | Easily separate from oil      |

### 3.2 Biodiesel production

The biodiesel conversions of palm oil with the different reaction method were shown in Table 2. The reaction conditions are Methanol to oil ratio 9:1, reaction time 3 h, catalyst loading 5%wt and reaction temperature 80 for stirring and 100 for static method. The result showed that Ca/ferrite-TEOS give the same conversion with pure CaO, but it is easier to be separated from biodiesel when compare with conventional CaO catalyst.

### Conclusion

The researchers successfully synthesized a magnetic core calcium oxide nano-catalyst (Ca/ferrite-TEOS) by using ferrite $\text{Fe}_3\text{O}_4$ core-shell. The core-shell ferrite was coated with calcium oxide, using co-precipitation method at pH 10. The calcium oxide on Ca/ferrite-TEOS catalyst form after calcined at 700°C for 5 h. The basic strength of samples is in range 9.8 – 15.0 and the morphology of magnetic core is present at 15 nm and is trapped in the core. The calcined Ca/ferrite-TEOS showed homogenous spherical shape with 92 nm. The IR of calcium oxide peak showed at 523 cm$^{-1}$. The EDX confirmed the present of Fe, Si and Ca on the catalyst. The Biodiesel-Conversion of used palm oil (acid value 1.2 mgKOH/g oil) gives over 90%.

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