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# Biodiesel Production from Palm Fatty Acids Distillate Using Tungstophosphoric Acid- and Cs-salt Immobilized-Silica

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## Abstract

$H_3PW_{12}O_{40}/SiO_2$ and $Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$ composites with controllable acid loadings (5 - 15 wt% loading) were prepared by direct co-condensation sol-gel methods in the presence of triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) copolymer. Biodiesel production from palm fatty acids distillate (PFAD) having 93 % free fatty acids (FFA), a residual product from the refining of crude palm oil was investigated using these heterogeneous catalysts. The results demonstrated that under the same reaction conditions the catalytic activity of $H_3PW_{12}O_{40}/SiO_2$ was higher than $Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$ due to higher acidity. A study on effects of reaction temperature, time and catalyst amount has been performed. The FAME content was 96.7 % at a temperature of 85 °C, 15 h reaction time, a molar ratio of methanol to PFAD at 12:1 and catalyst 15 wt% based on PFAD.

**Keywords:** Biodiesel, palm fatty acids distillate, tungstophosphoric acid, polyoxometalate, silica

## Introduction

Biodiesel is alkyl esters of fatty acids produced from vegetable oils and animal fats. There has been an increasing interest in biodiesel as a green and alternative fuel as a result of recent legislation that require a major reduction of vehicle emissions [1]. In Thailand, the government has promoted 5 % (v/v) biodiesel (B5) in the transport sector since 2005 and it plans on implementing the use of 100 % biodiesel (B100) in 2011. Biodiesel has not currently been commercialized all over the world due to the high feedstock cost. The biodiesel feeds containing high free fatty acid (FFA) are cheaper than oils without FFA. However the free fatty acid is saponified by the homogeneous alkaline catalyst, producing excess soap [2]. This problem can be circumvented by performing a two-step process. The first step is to reduce FFA by esterification of the FFA to alkyl esters in the presence of an acidic catalyst such as $H_2SO_4$, HF, $H_3PO_4$ and HCl, followed by the second step, transesterification using a base catalyst [3-5]. The replacement of these hazardous and polluting corrosive liquid acids by solid acid catalysts is one of the major demands of society [6,7]. Apart from recyclability and reusability, an ideal solid acid catalyst for biodiesel preparation should have high stability, numerous strong acid sites, large pores, hydrophobic surface and low cost. There have been reports of many solid acids: sulfated zirconia [8,9], mesoporous materials [10,11], sulfonated carbons [12,13], anionic resins [14], supported Nafion® resin [15], $WO_3/ZrO_2$ [16,17] and carbohydrate-derived catalysts [18].

Heteropoly acids (HPAs) are strong Bronsted acids, stronger than $H_2SO_4$ and catalyze esterification and transesterification reactions [19-21]. Moreover, HPAs were shown to be more resistant to proton solvation by water molecules than sulfuric or phosphoric acid [22]. The major disadvantages of HPAs as catalysts lie in their low thermal stability, low surface area (5 - 10 $m^2/g$) and solubility in polar media. HPAs can be made eco-friendly insoluble solid acid catalysts with high thermal stability and surface area by supporting them on suitable supports, e.g. silica [23,24], titania [25], zirconia [26], active carbon [27] and MCM-41 [28,29]. A promising approach to heterogenize polyoxometalates (POM) is occluding them into an inert matrix during the matrix synthesis or sol-gel method [30]. 12-Tungstophosphoric acid has high acidic strength, relatively high thermal stability compared with molybdenum HPAs. It is an efficient catalyst for esterification reactions of fatty acids for biodiesel production [31]. Although heteropoly acid dispersion onto high area supports can enhance the number of available acid sites [32], this cannot overcome the solubility issue during FFA esterification in methanol/ethanol [33]. It was reported that tungstophosphoric acid immobilized on silica (with 4.2 wt%) showed the highest catalytic activity for esterification of palmitic acid in methanol [24]. $Cs_xH_{3-x}PW_{12}O_{40}$ (x = 1-3) which is less soluble in methanol and water is capable of performing both esterification and transesterification reactions [21].

The cost of refined edible oil constitutes about 70 % of the biodiesel production cost [34]. Therefore, the use of inexpensive feedstocks may reduce the cost of biodiesel. Palm fatty acids distillate (PFAD) is a byproduct from production of consumable palm oil, with high FFA content (75 - 93 wt%) and can be used as a feedstock for the production of biodiesel. Lipid feedstocks such as greases that have a high free fatty acid (FFA) content have also been used [35,36].

In the present work, we develop efficient immobilized polyoxometalate catalysts for biodiesel production. $H_3PW_{12}O_{40}/SiO_2$ catalysts with different acid loadings were prepared via direct sol-gel co-condensation. $Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$ was also prepared and its catalytic activity compared with the acidic catalyst in order to see change in solubility and acidity of the catalyst. Both acidic and cesium catalysts were used to catalyze esterification of palm fatty acids distillate (93 wt% FFA) in methanol. Methanol was chosen because it is the most effective alcohol for esterification of fatty acid [37]. The solid acid catalysts were found to be effective for the esterification of PFAD with a fatty acid methyl ester (FAME) content of 96.7 %. The catalyst reusability offers a significant production cost advantage.

## Materials and methods

12-Tungstophosphoric acid, $H_3PW_{12}O_{40}$ was purchased from Wako Pure Chemical Industries Ltd. Tetraethylorthosilicate (TEOS) and triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) copolymer or P123 ($M$ = 5800) were purchased from Fluka. Palm fatty acids distillate (PFAD) was obtained from Chumporn Palm Oil Industry Public Company Limited. It consists of 93 wt% FFA (45.6 % palmitic, 33.3 % oleic, 7.7 % linoleic, 3.8 % stearic, 1.0 % myristic, 0.6 % tetracosenoic, 0.3 % linolenic, 0.3 % ecosanoic, 0.2 % ecosenoic, and 0.2 % palmitoleic acid) and the rest are triglycerides, diglycerides, monoglycerides and traces of impurities.

## Catalyst preparation

$Cs_{1.5}H_{1.5}PW_{12}O_{40}$ was prepared according to the literature method [38] by slowly adding dropwise aqueous cesium carbonate (0.47 M) to aqueous $H_3PW_{12}O_{40}$ (0.47 M). The precipitate obtained was aged for 20 h at 35 °C, followed by evaporation under vacuum at 45 °C and calcinated at 300 °C for 3 h. Its chemical composition was checked by chemical analysis of W and Cs.

The immobilized catalysts were prepared according to YH Guo *et al*. [39], by direct sol-gel co-condensation with a slight modification. The silica-gel source TEOS (3.26 g, 0.016 mol) was dissolved in ethanol (10 ml). $H_3PW_{12}O_{40}$ (5, 10 and 15 wt% based on TEOS) or $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ (10 wt% based on TEOS) were added. This mixture was added slowly to the ethanol solution (5 ml) of P123 (2.32 g, $4.0\times10^{-4}$ mol) at room temperature. The acidity of the mixture was controlled at pH ~1 by HCl. The mixture was stirred for 3 h. Then it was dried at 110 °C for 1 h, resulting in a clear gel. The hydrogel obtained was dehydrated at 45 °C for 48 h *in vacuo*. Removal of P123 was performed by calcination at 400 °C for 5 h.

The catalysts so obtained were characterized by their surface area, pore size and pore volume by the $N_2$ adsorption technique (BELSORP-mini). The X-ray powder diffraction pattern of catalysts was recorded to study the crystal structure by Rigaku, DMAX 2002/Ultima Plus diffractometer using Cu Kα radiation. Fourier-transform infrared spectra were recorded on a Nicolet FT-IR Impact 410 Spectrophotometer. The samples were made into a KBr pellet. Infrared spectra were recorded between 400 - 4000 cm$^{-1}$ in transmittance mode. The amount of W in the catalyst was measured by dissolving the catalyst in $H_2SO_4$/HF (1:1 v/v) and analyzing the solution using inductively coupled plasma (ICP) on Perkin Elmer model PLASMA-1000. Acidity of the catalysts was determined by n-butylamine titration. A 0.020 M solution of n-butylamine in toluene was used for estimation. The catalyst weighing 0.5 g was suspended in this solution for 24 h and excess base was titrated against trichloroacetic acid using neutral red as an indicator. This gives the total acidity of the catalyst. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker NMR400DRX spectrometer. $^1$H NMR spectra were recorded at 400 MHz and referenced to the proton resonance resulting from incomplete deuteration of the deuterated chloroform (δ 7.26).

**Esterification of palm fatty acids distillate (PFAD)**

The catalytic experiments were carried out in a Parr reactor. The reactor was loaded with 5 g palm fatty acids distillate (PFAD), and the appropriate amount of methanol and catalyst. The mixture was stirred at various temperatures and time with stirring speed at 500 rpm. Then the catalyst was separated by centrifugation. The top phase (methanol) was removed by evaporation. The FAME content was determined using $^1$H NMR spectroscopy measuring the percent conversion to the ester by the ratio of the area of peaks associated with the methyl ester (3.7 ppm) and methylene group protons (2.3 ppm).

**Catalyst reusability and leaching tests**

The catalyst was separated from the reaction mixture by filtration, washed with hexane and methanol to remove methyl esters on the surface. It was dried at 100 °C and calcinated at 280 °C for 3 h, then used in subsequent catalytic cycles. For the leaching test, after the run, the amount of polyoxometalate: $H_3PW_{12}O_{40}$ or $Cs_{1.5}H_{1.5}$ $PW_{12}O_{40}$ remained on silica was measured by ICP.

$$\text{Leaching (\%)} = \frac{\text{initial amount of polyoxometalate - remaining amount of polyoxometalate}}{\text{initial amount of polyoxometalate}} \times 100$$

## Results and discussion

The immobilized catalysts were prepared by simultaneous hydrolysis and condensation of tetraethoxysilane (TEOS) with $H_3PW_{12}O_{40}$ and $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ in the presence of a template surfactant, Pluronic P123 followed by subsequent steps of hydrothermal treatment and template removal. This method of synthesis differs from the conventional sol-gel synthesis. It can enhance dispersion of acid over a high surface area $SiO_2$ support and prevent the Keggin structure decomposition, and would retain the intrinsic acidity of the HPA [40]. The removal of P123 was done by calcination in order to inhibit the loss of the Keggin unit.

**Characterization of catalysts**

Diffraction peaks of the crystalline structure of $H_3PW_{12}O_{40}$ and $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ are observed at $2\theta$ = 3 - 60° (**Figure 1**). The Cs-salt shows sharper peaks, revealing higher crystallinity. The XRD patterns of the $H_3PW_{12}O_{40}/SiO_2$ with different acid loadings (5, 10 and 15 wt%) are shown in **Figure 2**, only one broad peak appears. There are no diffraction patterns of $H_3PW_{12}O_{40}$. A similar XRD pattern to $H_3PW_{12}O_{40}/SiO_2$ was obtained for $Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$(10 wt%). No related peaks to polyoxometalates were observed suggesting a high dispersion as a non-crystalline form or low amounts of polyoxometalates [38].

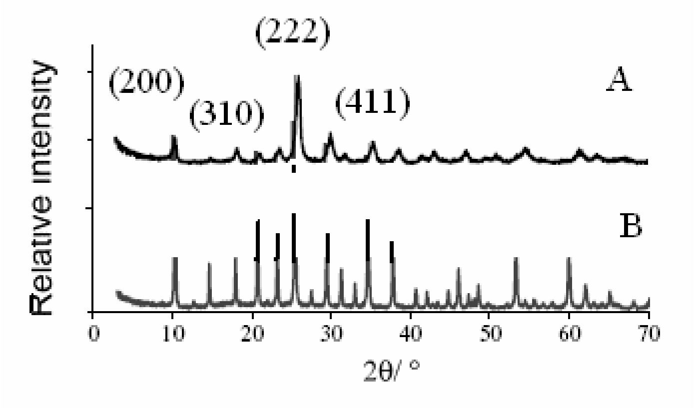

**Figure 1** XRD patterns of (A) $H_3PW_{12}O_{40}$ and (B) $Cs_{1.5}H_{1.5}PW_{12}O_{40}$.

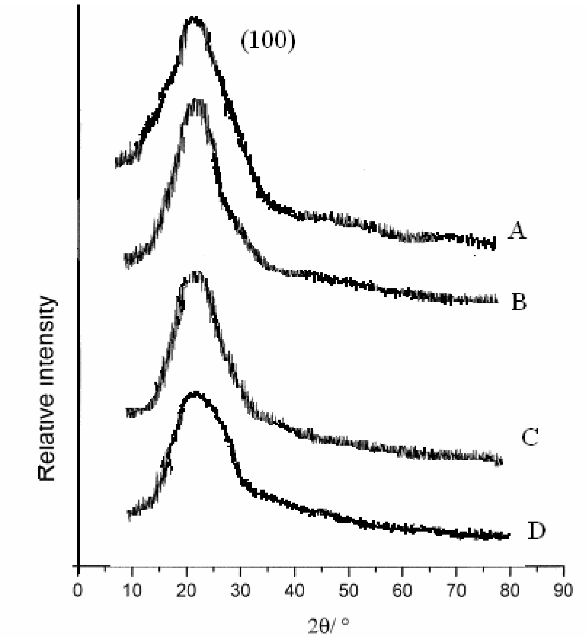

**Figure 2** XRD patterns of (A) 5 wt%, (B) 10 wt%, (C) 15 wt% acid loading $H_3PW_{12}O_{40}/SiO_2$ and (D) $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ (10 wt%).

**Figure 3** shows FTIR spectra of $H_3PW_{12}O_{40}$ and $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ between 1,400 - 400 cm$^{-1}$. In **Figure 4**, the spectra of the immobilized catalysts were compared with silica. The bands at 802 and 463 cm$^{-1}$ can be assigned to Si-O-Si stretching and Si-O-Si bending, respectively. The bands of polyoxometalates included on mesoporous silica are found at 1,100 - 1,000 cm$^{-1}$ and overlap the bands of the silica matrix. However, IR bands of polyoxometalates can be observed at 896 - 889 and 978 - 983 cm$^{-1}$, assignable to the W=O (terminal oxygen) and W-O-W (corner-sharing oxygen). The observed vibration peaks of the Keggin structure suggest that the Keggin structures of these catalysts are preserved [41]. The vibration peaks were shifted, indicating interaction between the Keggin unit and the support [38]. FTIR data of the polyoxometalates and the immobilized catalyst are shown in **Table 1**.

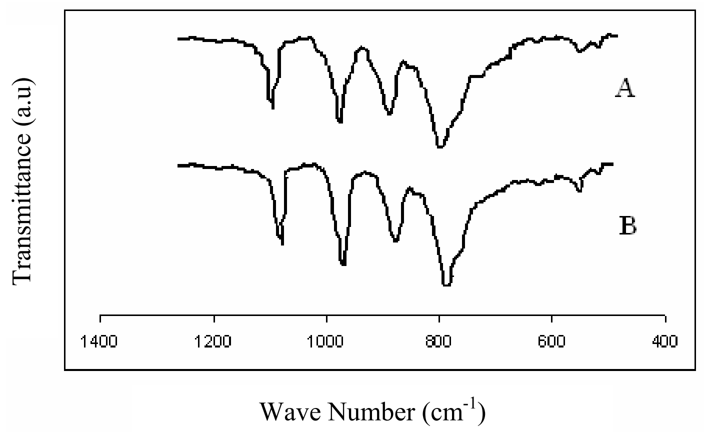

**Figure 3** FTIR spectra of (A) $H_3PW_{12}O_{40}$ and (B) $Cs_{1.5}H_{1.5}PW_{12}O_{40}$.

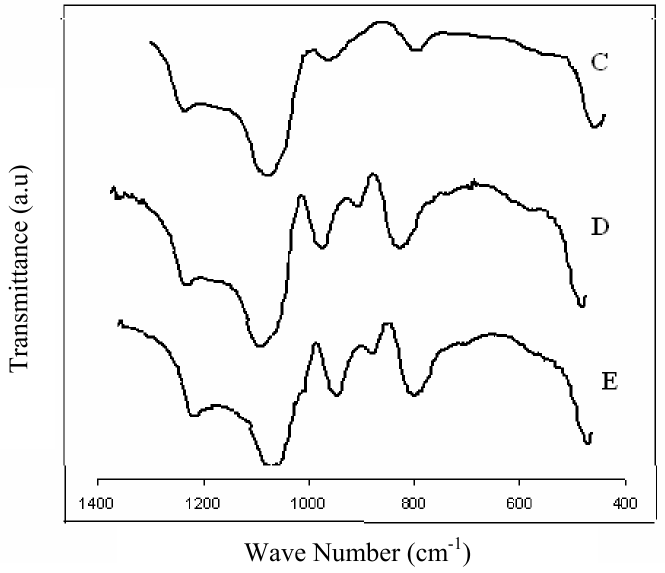

**Figure 4** FTIR spectra of (C) $SiO_2$, (D) $H_3PW_{12}O_{40}$(10 wt%)/$SiO_2$ and (E) $Cs_{1.5}H_{1.5}PW_{12}O_{40}$(10 wt%)/$SiO_2$.

**Table 1** IR data for the catalysts.

| Catalyst | Wavenumber ($cm^{-1}$) | | | |
|---|---|---|---|---|
| | P or Si-O | W=$O_t$ | W-$O_c$-W | W-$O_e$-W |
| $H_3PW_{12}O_{40}$ | 1080 | 986 | 898 | 800 |
| $H_3PW_{12}O_{40}$/$SiO_2$ (5 - 15 wt%) | 1086 | 983 | 896 | 804 |
| $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ | 1077 | 983 | 890 | 789 |
| $Cs_{1.5}H_{1.5}PW_{12}O_{40}$/$SiO_2$ (10 wt%) | 1074 | 978 | 889 | 787 |

$O_t$ (terminal oxygen), $O_c$ (corner-sharing oxygen), $O_e$ (edge-sharing oxygen)

The physical properties (surface area, pore volume and pore diameter) of $H_3PW_{12}O_{40}/SiO_2$ and $Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$ catalysts as well as the polyoxometalates and silica are presented in **Table 2**. The size of the Keggin polyoxometalate anion is about 1 - 1.2 nm. Therefore $H_3PW_{12}O_{40}$ acid impregnated into the mesoporous silica was distributed on all the surfaces of the silica and filled in the pores, resulting in blocked up pores of silica and, therefore, a lower surface area, pore volume and pore diameter. The $N_2$ adsorption-desorption isotherms at 77K for $H_3PW_{12}O_{40}/SiO_2$ and $Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$ (10 wt% loading) were measured and shown in **Figure 5**. The $N_2$ adsorption-desorption isotherms are Type IV, which is indicative of a well-distributed mesostructure material [39]. The formation of the mesopores originates from the porous structure of the silica particle gels obtained from hydrolysis of TEOS under acidic conditions.

### Catalytic activity testing by esterification of palm fatty acids distillate (PFAD)

Esterification of PFAD was carried out using $H_3PW_{12}O_{40}/SiO_2$ and $Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$ catalysts. Results are shown in **Table 3**.

**Table 2** The physical properties of immobilized catalysts.

| Catalyst | Acid loading (wt%) | BET surface area ($m^2/g$) | Pore volume ($cm^3/g$) | Pore diameter (nm) |
|---|---|---|---|---|
| $H_3PW_{12}O_{40}/SiO_2$ | 5 | 396 | 0.21 | 2.5 |
| | 10 | 335 | 0.18 | 2.3 |
| | 15 | 260 | 0.14 | 2.1 |
| $Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$ | 10 | 320 | 0.17 | 2.4 |
| $H_3PW_{12}O_{40}$ | - | 4 | 0.08 | 1.1 |
| $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ | - | 14 | 0.10 | 1.2 |
| $SiO_2$ | - | 485 | 0.26 | 2.8 |

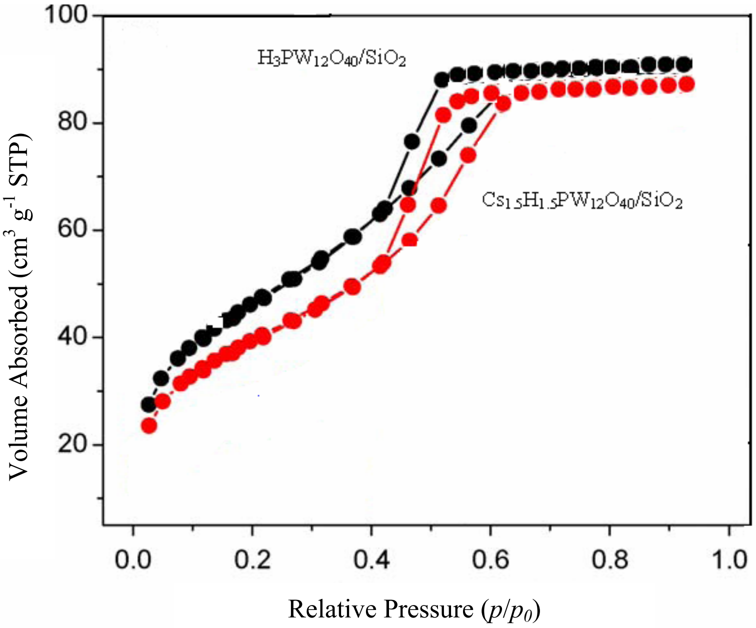

**Figure 5** Nitrogen adsorption-desorption isotherms of $H_3PW_{12}O_{40}/SiO_2$ and $Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$ (10 wt% loading).

**Table 3** Activity of immobilized catalysts for esterification of PFAD.

| Catalyst | Loading (wt%) | Acidity (mmol/g) | FAME (wt%) | Leaching (%) |
|---|---|---|---|---|
| $H_3PW_{12}O_{40}/SiO_2$ | 5 | 0.4 | 65.2 | 0 |
| | 10 | 0.6 | 77.6 | 1 |
| | 15 | 0.7 | 83.1 | 5 |
| $Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$ | 10 | 0.1 | 66.0 | 0 |

Reaction conditions: PFAD 5 g, 12:1 molar ratio of methanol to PFAD, catalyst 10 wt% based on PFAD, at 75 °C, 12 h.

The result shows that the $H_3PW_{12}O_{40}/SiO_2$ catalysts exhibit higher activity with higher acid loading, more acidic sites result in higher FAME content. The 15 wt% acid loading shows the highest activity (83.1 % FAME). However, the result from the ICP analysis shows 5 % acid leaching from the silica support (or 14.25 wt% remained) whereas the catalysts with lower loadings (5 and 10 wt%) showed little leaching. Therefore for the 15 wt% $H_3PW_{12}O_{40}/SiO_2$ catalyst there may also be some contribution of homogeneous reaction due to acid leaching. No leaching was found for $Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$ due to the lower solubility of the Cs salt in methanol. However with the same loading (10 %), $H_3PW_{12}O_{40}/SiO_2$ gave a higher FAME content (77.6 %) than $Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$ (66.0 %), this is due to the higher acidity of the former. A similar result was previously reported on esterification of palmitic acid over $H_4SiW_{12}O_{40}$ compared to Cs-doped $H_4SiW_{12}O_{40}$ [42]. Therefore, the $H_3PW_{12}O_{40}/SiO_2$ (10 wt%) catalyst was chosen for further experiments to investigate the effect of reaction time and amount of catalyst.

In order to complete the esterification reaction, sufficient contact time must be provided. **Figure 6** shows the effect of reaction time on FAME content over the $H_3PW_{12}O_{40}/SiO_2$ (10 wt% loading) catalyst using 12:1 molar ratio of methanol to PFAD, catalyst 10 wt% based on PFAD at 75 °C. %FAME amount increases with increasing reaction time. At 9, 12 and 15 h, wt% FAME are 70.3, 77.6 and 86.1 %, respectively. At longer time (18 h), there was no further increase in the amount of FAME. Therefore, 15 h is sufficient for complete esterification under these conditions.

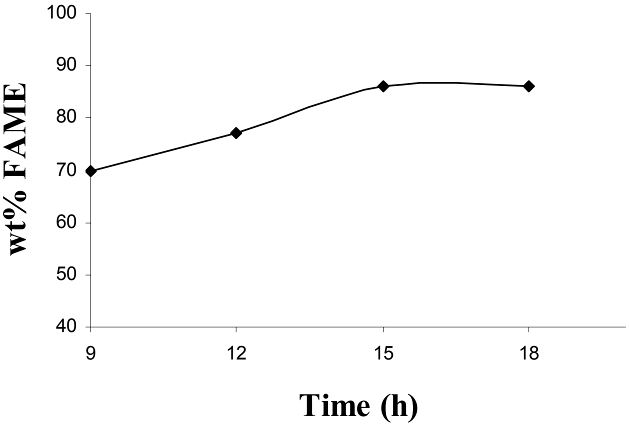

**Figure 6** Effect of reaction time on wt% FAME at 75 °C, 12:1 molar ratio of methanol to PFAD and 10 wt% $H_3PW_{12}O_{40}/SiO_2$ (10 wt% loading) catalyst.

Temperature is one of the important variables for acid-catalyzed esterification because the rate of reaction is strongly influenced by the reaction temperature. Reaction temperature was varied in the range 65 - 95 °C (**Figure 7**). The FAME content increased with increasing temperature. The FAME content increased from 86.1 to 90.0 % when the temperature was increased from 75 to 85 °C at 15 h, this shows that the time can be shortened with an increase in temperature. However, it was reduced at 95 °C. There was increasing darkness in the color of the product at this temperature.

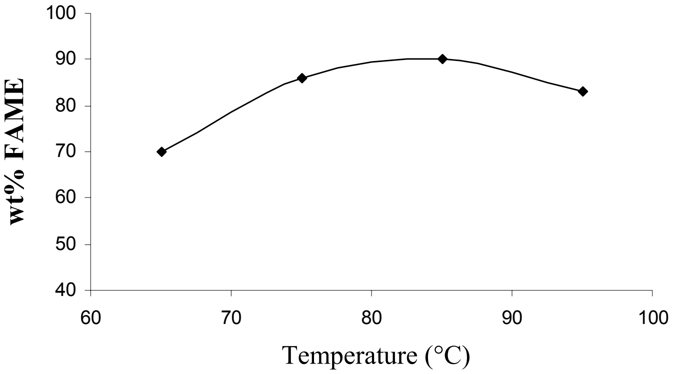

**Figure 7** Effect of reaction temperature on wt% FAME at 15 h, 12:1 molar ratio of methanol to PFAD and 10 wt% $H_3PW_{12}O_{40}/SiO_2$ (10 wt% loading) catalyst.

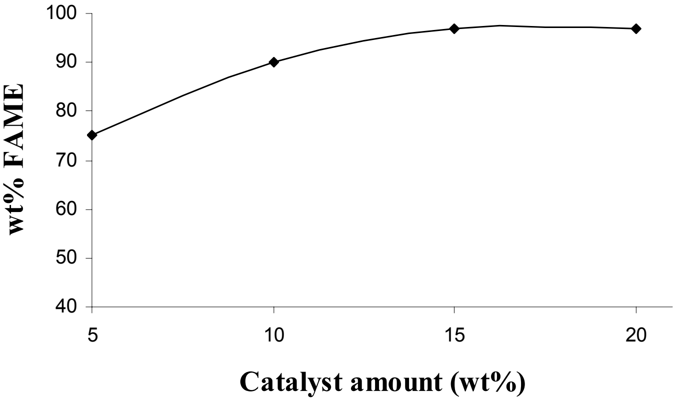

**Figure 8** Effect of catalyst amount on wt% FAME at 85 °C, 15 h, and 12:1 molar ratio of methanol to PFAD and $H_3PW_{12}O_{40}/SiO_2$ (10 wt% loading) catalyst.

**Table 4** Fuel properties of biodiesel obtained from esterification of PFAD.

| Properties | This work | Thai standard | ASTM D6751-02 |
|---|---|---|---|
| Pour point (°C) | 13 | - | −15 to 10 |
| Cloud point (°C) | 14 | - | −3 to 12 |
| Ester content (wt%) | 96.7 | 96.5 min | - |
| Copper strip corrosion | 1 | 1 max | 3 max |

The amount of catalyst used in the process was varied (5 - 20 wt% catalyst based on PFAD). In **Figure 8** it was found that the FAME content increased with increasing catalyst amount, which could be attributed to the reason that more catalyst would provide more active reaction sites. At 85 °C and 15 h, 12:1 molar ratio of methanol to PFAD, the appropriate amount of catalyst was 15 wt% as it gave maximum amount of FAME (96.7 %). There was no improvement in FAME content when the amount of catalyst was higher than 15 wt%.

After the catalyst was separated, washed and calcinated, it was reused with fresh PFAD and methanol. The results revealed little loss in the activity after three recycles (94.5 % FAME). The catalyst synthesized in this work shows higher stability (little leaching of acid catalyst from the support, as shown in **Table 3**) compared to those reported in the literatures that show leaching of active species from the support [43-45].

The final product is a light brown material meeting the requirements of the Thai biodiesel standard, as shown in **Table 4**.

## Conclusion

$H_3PW_{12}O_{40}/SiO_2$ and $Cs_{1.5}H_{1.5}PW_{12}O_{40}/SiO_2$ prepared by direct sol-gel co-condensation were shown to be efficient catalysts for the esterification of palm fatty acids distillate with methanol to produce biodiesel. At 85 °C, a reaction time 15 h, molar ratio of methanol to palm fatty acids distillate of 12:1, and catalyst 15 wt% based on PFAD, 96.7 % FAME was obtained over $H_3PW_{12}O_{40}/SiO_2$ with 10 wt% acid loading. The main advantages of using a heterogeneous catalyst are that no washing step is required for biodiesel purification and the catalyst can be easily separated and reused. The fuel properties of the biodiesel so obtained meet Thai biodiesel standards.

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