Renewable Energy 62 (2014) 10–17

Contents lists available at SciVerse ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

# Transesterification of crude Jatropha oil by activated carbon-supported heteropolyacid catalyst in an ultrasound-assisted reactor system

Ali Sabri Badday [1], Ahmad Zuhairi Abdullah*, Keat-Teong Lee [1]

School of Chemical Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

A R T I C L E I N F O

*Article history:*
Received 12 September 2012
Accepted 25 June 2013
Available online 15 July 2013

*Keywords:*
Biodiesel
Tungstophosphoric acid
Activated carbon
Ultrasound-assisted process
Jatropha oil
Water content

A B S T R A C T

Transesterification of crude Jatropha oil in presence of tungstophosphoric acid (TPA) supported on activated carbon (AC) using ultrasound-assisted process was investigated. The generated catalysts were characterized for physical and chemical properties to examine the effects of different TPA loadings (15%, 20%, 25% w/w). The catalysts were then used in the transesterification of Jatropha oil with high free fatty acid content. The catalyst with 20% TPA loading achieved the best methyl ester yield, achieving 87.33% in just 40 min. The quality of the feed stock was varied by increasing the water content and FFA content to test the tolerance of the catalysts towards these parameters separately. The catalyst showed good water tolerance to a limit of 1% w/w and proven to be insensitive to the increment of FFA in the feed stock. The catalyst was also investigated for possible reusability and TPA leaching under ultrasonic conditions.

## 1. Introduction

Biodiesel is considered as an interesting green energy resource as it is a renewable, biodegradable and non-toxic material. The most successful method for producing the mixture of alkyl esters which form the biodiesel is by transesterifying vegetable oils or animal fats with suitable alcohol [1]. This process involves consecutive reaction steps in that lead to the conversion of a triglyceride to fatty acid alkyl esters and glycerin as the main coproduct. Generally, excess alcohol is used to favor the forward reaction and the reaction is carried out in the presence of a suitable catalyst [2]. However edible vegetable oils such as palm oil, sunflower oil, rapeseed oil and soybean oil are considered as the most suitable feed stock for biodiesel production [3]. Recently, non-edible oils such as Polanga oil, Karanja oil, and Jatropha oil attracted great attention as feed stocks in biodiesel production [4,5].

Jatropha oil is a source of triglyceride which possesses good potential for biodiesel production as it is a non-edible oil and has no conflicting interest when used for edible purposes [4]. However, this type of oil has high FFA and water content that present some drawbacks when base catalysts are considered for biodiesel production process. Therefore, possibility for the application of highly active solid acid catalysts should be explored to convert this oil to biodiesel. In this respect, Acid catalyzed systems seem to be an interesting research field to be investigated to improve the biodiesel production from non-edible triglycerides resources.

Base catalysts have a great limitation to be used with wide range of feed stock. As the percentage of free fatty acids in vegetable oil exceeds 1%, a side reaction will occur consuming the catalyst and forming metal soap [6,7]. So homogenous acid catalysts are suggested to catalyze the reaction due to its insensitivity towards high FFA content coupled with its ability to catalyze esterification and transesterification simultaneously [8,9]. However, they generally require high reaction temperature and high oil to alcohol molar ratio as the reaction rate is relatively lower, especially in the case of solid acid catalysts. These days, solid acid catalysts attract researchers' attention due to their better tolerance towards high FFA and water content. At the same time, they can be easily separated from the reaction mixture after the reaction [10,11]. Both esterification and transesterification reaction can occur simultaneously neglecting the needs for two-step biodiesel production [12]. This will positively affect the production cost as no further requirement for unnecessary extra equipment is expected. Solid acid catalysts such as zirconia [13], sulfonic acid-functionalized silica [14], carbon-based solid acid catalyst [15] and heteropolyacids (HPAs) [16] have been reported for biodiesel production from various triglyceride sources.

---

* Corresponding author. Tel.: +60 4 5996411; fax: +60 4 5941013.
*E-mail addresses:* chzuhairi@eng.usm.my, azuhairi@yahoo.com (A.Z. Abdullah).
[1] Tel.: +60 4 5996411; fax: +60 4 5941013.

0960-1481/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.renene.2013.06.037

Besides its great water tolerance and insensitivity towards FFA, HPAs possess strong Brönsted acidity and high proton mobility [17]. HPAs such as $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4Si–Mo_{12}O_{40}$ have been used to catalyze a wide range of acid-catalyzed reactions including vegetable oil transesterification for biodiesel production. This is because the acid sites are more identical and easier to manage compared to those in other acid catalysts [18]. Thus, this group of materials provides interesting option for use in biodiesel production process.

Biodiesel production using HPAs as homogenous catalysts has been investigated by Morin et al. [16]. The activity of the studied HPAs was found to be comparable to those of $H_2SO_4$ and $H_3PO_4$. Due to the solubility of HPAs in methanol and ethanol, Zhang et al. [18] used a derived Cs salt of HPAs with the objectives of reducing their the solubility while at the same time increasing the surface area of the parent HPA. Various types of supports have also been used to immobilize HPAs such as silica [19], zeolites [20] and activated carbon [21] to increase the low surface area and to create heterogeneity for HPAs. For example, Katada et al. [22] successfully improved the activity of $H_4PNbW_{11}O_{40}/WO_3–Nb_2O_5$ catalyst used in the transesterification process of triolein and ethanol. Other acid derived solid catalyst has been investigated by Sunita et al. [23]. They conducted a study to demonstrate the activity of zirconia-supported isopoly and heteropoly tungstate catalysts for biodiesel synthesis. Generally, good catalytic activity was demonstrated by the catalysts. However, suitable modification on the process set up is deemed necessary to significantly increase the low reaction rate resulted by the immiscible nature of the reactants.

Ultrasonic technology is an attractive and effective procedure to solve the problems related low reaction rate in biodiesel production. This problem stems from the poor contact between the reactants due to their mutual immiscibility. The use of ultrasonic irradiation in the process can enhance the mass transfer rate between the reactants leading to significant improvement in the reaction rate [24]. Application of ultrasound in biodiesel production process has been demonstrated to accelerate the reaction leading to significant reduction in reaction time with some improvement in the production yield [25,26]. The use of ultrasonic energy in base-catalyzed biodiesel production or in two stage process has been investigated and reported in literature [27,28]. However, the use of heterogeneous acid catalyst under ultrasonic conditions stills an immature research area that requires further investigation. As solid acid catalysts are relatively less active than base catalysts, accelerating the reaction by means of an ultrasonic irradiation will provide interesting opportunity towards a more productive and economical biodiesel production process.

In this study, the ultrasonic-assisted transesterification of crude Jatropha oil with methanol over tungstophosphoric acid (TPA) ($H_3PW_{12}O_{40}$) immobilized on activated carbon has been investigated. Particular focus has been given to the effects of TPA loading on the characteristics of the catalyst and the subsequent influences on the transesterification reaction. Influence of FFA and water content in oil feed stock has been elucidated to highlight the rule of the prepared catalyst on conducting significant transesterification for high FFA systems. Finally, the stability of the catalyst towards leaching and potential for the reusability of the catalyst under the ultrasonic irradiation conditions has been demonstrated.

## 2. Experimental

### 2.1. Reagents and materials

Tungstophosphoric acid ($H_3PW_{12}O_{40}$) active component, abbreviated as TPA in this work was purchased from Merck (Malaysia) while activated carbon (AC) support was purchased from Galcon Carbon Corporation (USA). The AC was first ground to mean particle sizes between 250 and 500 μm. Crude Jatropha oil as the source of triglyceride in this study was supplied by Telaga Madu Resources (Malaysia). The properties of the crude Jatropha oil, FFA content and water content are given in Table 1. Methanol that was used in the transesterification reaction was supplied by Thermo Fisher Scientific Inc. (USA). Ethanol (for catalyst preparation) and n-hexane (for product analysis) were purchased from Merck (Malaysia). Meanwhile, reference fatty acid methyl ester (FAME) standards were supplied by NuChek Prep. Inc. (Australia).

### 2.2. Catalyst preparation

In order to prepare the supported catalyst, a pretreatment was first conducted by washing the support with 0.1 M NaOH solution, followed by the second treatment with 0.1 M HCl. They were performed to remove any soluble alkaline and acidic impurities from the AC [29]. The supported catalysts were prepared by dissolving the desired amounts of TPA in a mixture of deionized water and ethanol solution (50:50 v/v). Wet impregnation method was then adopted by contacting the support with the solution (4 ml/g support) for 72 h under constant shaking. Then, excess solution was removed by means of a rotary evaporator and the catalyst was subsequently washed excessively with deionized water followed by drying over night. The dry catalyst was then calcined at 453 K in air for 4 h [30].

### 2.3. Catalyst characterization

The surface properties of AC and other catalysts were examined by means of a Micrometrics ASAP 2020 surface analyzer. FT-IR spectra of the supported TPA-AC catalysts were obtained using a Perkin–Elmer FTIR spectrophotometer. The surface morphology and TPA distribution over the carbon support was observed using an SEM unit (Oxford INCA/ENERGY-350) equipped with an energy dispersive X-ray analysis (EDAX) system. Surface acidity of the AC and the immobilized catalysts was determined using an acid-base titration [31].

### 2.4. Ultrasound-assisted transesterification process

The ultrasound-assisted transesterification process was conducted in a three-neck glass batch reactor placed in a water bath to maintain the reaction temperature. A condenser was attached to the reactor to contain the evaporated methanol and condense it back to the reaction vessel. Ultrasonication was achieved by means of an ultrasonic processor with a probe type transducer. The ultrasonic energy was supplied using a Branson (USA) ultrasonic processor capable of generating a frequency of 20 kHz with a highest power of 400 W.

Blank experimental runs were first carried out in the absence of catalyst or ultrasonic irradiation. The absence of catalyst was tested by providing ultrasonic irradiation at 75% of the maximum power with a methanol/oil ratio of 20 for 60 min. The same conditions were used in the presence of activated carbon at a loading of 4%. An

**Table 1**
Properties of Jatropha oil used in this study.

| Property | Value |
|---|---|
| Density (kg/m$^3$) | 921 |
| Viscosity (cSt) | 38.12 |
| Molecular weight | 870 |
| Water content (w %) | 0.161 |
| FFA content (w %) | 10.5 |

experimental run under mechanical stirring was also performed under the same reaction conditions in the presence of catalyst.

In a typical experimental run, the desired amount of oil was transferred to the reactor and placed in the water bath until it reached the desired reaction temperature. Then, a required preheated amount of methanol was added to the oil at a molar ratio 20:1 followed by the desired amount of catalyst (4% wt/wt oil). At this point, ultrasonification was started and the condenser attached to recover the evaporated methanol. Ultrasonic energy was supplied in a discrete pattern with 10 s on and 3 s off with the ultrasonic amplitude set at 75% of the maximum power. After the desired reaction time (60 min), the reaction mixture was quenched and the excess methanol was distilled out. The reaction mixture was then separated into two layers by centrifugation at 3000 rpm for 20 min. The upper FAME layer was then collected for GC analysis.

For studying the effect of reaction time, the same previous procedure was conducted at different time intervals between 30 min and 120 min. The effects of water content in Jatropha oil was studied by adding the desired amount of water to the oil at various weight ratios (1%, 2%, 3%, 4% w $H_2O$/w oil). Meanwhile, testing of FFA effects was conducted by adding the desired amounts of FFA to the Jatropha oil under heating and continuous stirring. For all experimental runs, the water bath temperature was fixed at about 56 °C. Due to heat energy that was also generated by the ultrasonic wave, the reaction temperature was steadily maintained at 65 ± 1 °C.

In order to study the leaching of $PW_{12}O_{40}^{3-}$ heteropoly anion into the polar reaction mixture and to examine the effect of ultrasonic irradiation on the catalyst stability, an experiment similar to the “hot-filtration experiment” was conducted [19,21]. The catalyst was first mixed with methanol and ultrasonically treated under the reaction conditions. After the desired reaction time, the solid catalyst was filtered out and a desired amount of oil was added to the methanol. The reaction was then performed without the use of any catalyst for the optimum reaction time and the product was collected for analysis. All the experiments were carried out in the presence of air under atmospheric pressure.

### 2.5. Product analysis

A gas chromatograph (Agilent tech 7890 A GC systems) equipped with a capillary column (Agilent Technologies, Inc. 19091 J-413 hp-5) were used for product analysis. The system was equipped with a flame ionization detector (FID) and helium was used as the carrier gas. The analysis of FAME for each reaction mixture was carried out by dissolving the sample in n-hexane according to the desired dilution factor and 1 μl of the mixture was then injected into the GC.

## 3. Results and discussion

### 3.1. Catalyst characterization

Surface characteristics of AC and the TPA-AC catalysts combined with the surface acidity data are summarized in Table 2. Tungstophosphoric acid itself is a non-porous material and the surface area is reported to be only about 1–2 $m^2/g$ [30]. The BET surface area of the AC support used in this research was 750 $m^2/g$ and the area contributed by micropores was about 73% of the total surface area. It is noted from the table that immobilization of TPA on AC resulted in slight reductions in surface area, microporous volume and total porous volume. The magnitude of reduction was found to increase with increasing amount of TPA in the catalyst. This could be attributed to the partial blockage of pores by the active species. As a highly porous material, AC could accommodate high loading of TPA without experiencing significant drop in its porosity. A reduction in surface area after tungstophosphoric acid incorporation into an activated carbon was also observed Oball et al. [30].

**Table 2**
Physical properties of AC and TPA catalysts.

| Sample | Surface area ($m^2/g$) | | Pore volume ($cm^3/g$) | | Surface acidity ($\mu mol/g_{cat}$) |
|---|---|---|---|---|---|
| | BET | Micropore | Total | Micropore | |
| AC | 750 | 547 | 0.47 | 0.29 | 520 |
| TPA15-AC | 651 | 491 | 0.41 | 0.26 | 1530 |
| TPA20-AC | 621 | 467 | 0.39 | 0.25 | 1570 |
| TPA25-AC | 612 | 462 | 0.38 | 0.24 | 1690 |

The calculated values of surface acidity as shown in Table 2 reveal that AC was a material with low surface acidity and the catalysts showed significantly higher acidity with the increasing loading of TPA. As significant drop in the surface area was not observed, the acid sites were deemed accessible for reactants during the reaction which could bring about the desirable effect on the reaction rate. These results concluded that loading of TPA into the catalyst successfully introduced significant number of strong acid sites on the surface of the support material to act as good solid acid catalysts.

The FT-IR spectra for supported TPA-AC catalysts are shown in Fig. 1. The spectra of pure TPA showed four major bands. These bands are attributed to the stretching modes of oxygen to phosphorous and tungsten in the adsorption mode of the Keggin ion $(PW_{12}O_{40})^{-3}$. Bands at 800 $cm^{-1}$ (W–O–W at the edge), 890 $cm^{-1}$ (W–O–W at the corner), 980 $cm^{-1}$ (W=O) and at 1080 $cm^{-1}$ (P–O) can be detected for the Keggin ion which were in agreement with the results of Ferreira et al. [21]. Based on Fig. 1, no characteristic band could be detected for AC while for the immobilized catalysts, three major bands could be detected with increasing intensity with the amount of TPA loaded. For these bands, some shifts in their positions were noticed due to the new interactions that occurred between AC and TPA. The achieved results showed good agreements with those reported by Oball et al. [30] and Ferreira et al. [21]. These results suggested the successful synthesis of TPA-AC catalysts without excessive loading of active component that could subsequently affect the activity.

The SEM images of AC and the supported catalysts are shown in Fig. 2. The micro images of the catalysts were obtained using the fresh catalysts before being used in the transesterification reaction.

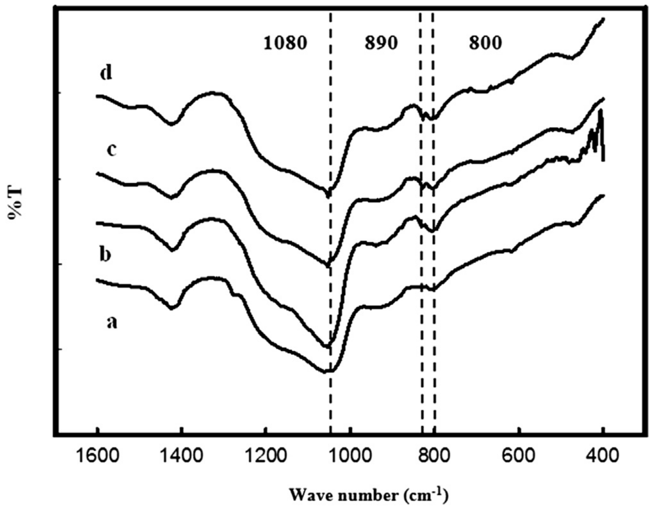


**Fig. 1.** FT-IR spectra for (a) AC (b) TPA15-AC (c) TPA20-AC (d) TPA25-AC.

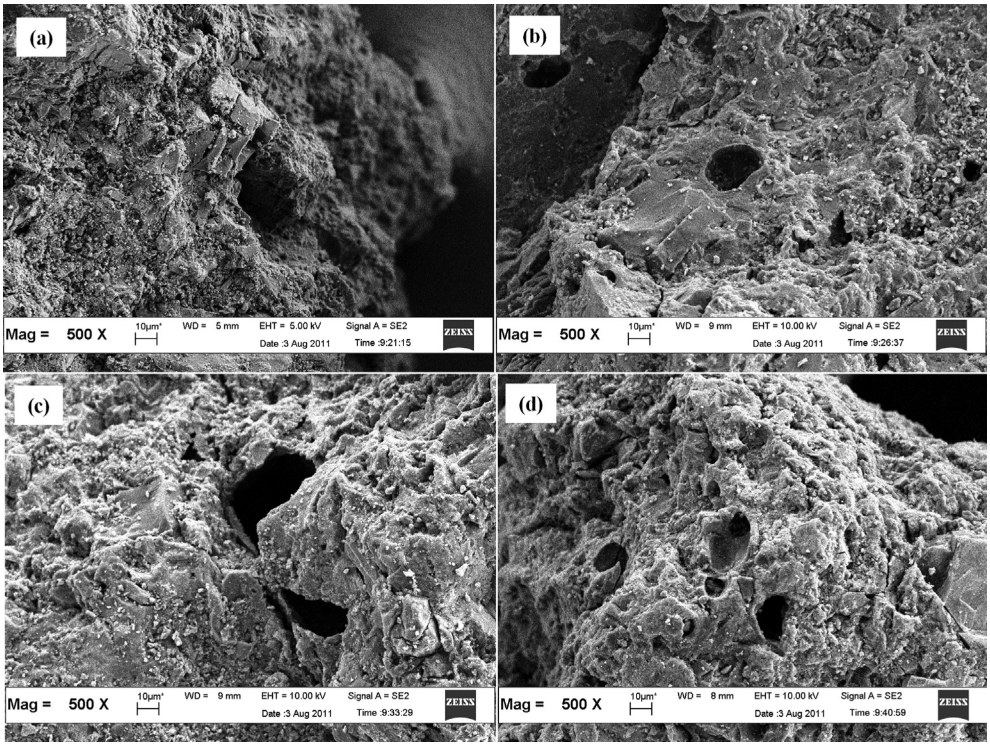


**Fig. 2.** Scanning electron micrographs (SEM) images of (a) AC (b) TPA15-AC (c) TPA20-AC (d) TPA25-AC.

The acid functionalized catalysts showed irregular distributions of the TPA on the AC surface. The deposition of TPA on the surface of AC not only responsible for the partial reduction on the surface area as the amount of the TPA increased but also resulted in the activity increase for the catalysts.

The EDAX results for the support and the immobilized catalysts can be seen in Fig. 3. These results prove that the existence of metallic materials attached to AC surface. EDAX result for AC correctly gave only carbon element while for the other catalysts, the presence of the Keggin anion $(PW_{12}O_{40})^{-3}$ can be detected. It can be concluded from these results that the amount of tungsten, oxygen and phosphorous increased with the increasing loading of TPA on AC. This, in turn, increased the catalyst activity in the transesterification of Jatropha oil.

### *3.2. Catalytic activity*

#### *3.2.1. Blank experiments*

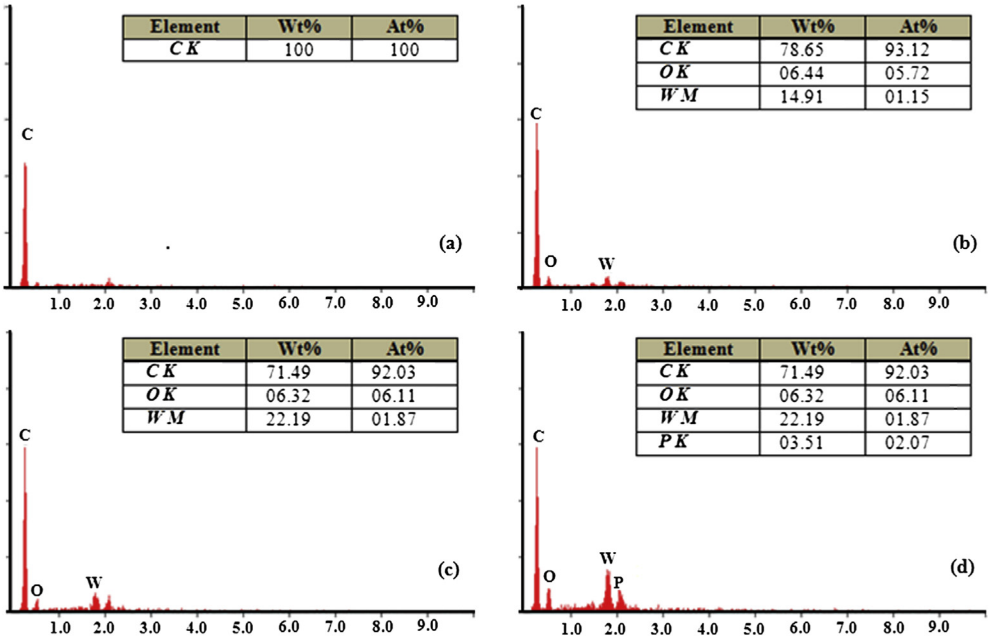
The results of blank experimental runs revealed that transesterification reaction did not significantly occur within a short reaction time of 60 min with the presence of AC only or without the use of any catalyst (Fig. 4). This was mainly due to the absence of acid active sites to catalyze the reaction. It also led to the conclusion that a suitable catalyst was indeed essential to achieve significant reaction. However, it is inaccurate to conclude that ultrasonic irradiation could activate the catalyst. Actually, this external energy could accelerate the reaction by improving mass transfer between the two immiscible reactants. Conducting the reaction without the use of ultrasound (mechanically stirred) also resulted in negligible reaction due to the short reaction time coupled with the poor catalytic activity of the solid acid catalysts. It has been reported that conventional acid catalyzed reactions requires long reaction time (5–6 h) due to the slow reaction rate [5]. Meanwhile, base-catalyzed process could be carried out with relatively shorter reaction times (2–3 h) [4,32].

It has been generally reported that higher molar ratio of methanol to oil can be used in order to prevent backward reaction to achieve higher biodiesel yield [3,5,15]. However, the methanol to oil ratio used in this study was already high i.e. at 20:1. High ratio also means that the concentration of Jatropha oil as the limiting reactant in the system is low to bring about undesired effect as far as the reaction rate is concerned. As such, certain suitable level of this ratio should be used. In this study, effect of reactants' ratio was beyond the main scopes to be investigated. However, it is agreeable that this variable could also affect certain behaviors of the reaction but discussion on this matter will be reported separately.

The activity of the AC-based TPA catalysts was found to be slightly better than that reported previously using alumina-based TPA catalysts [33]. For comparison, 20 wt. % TPA loading in alumina led to a FAME yield of about 50% in 60 min while the yield simply exceeded 70% in this study. Differences in the activity could be associated with the significantly higher surface area of the AC-based catalyst used in the present study (93 $m^2$/g versus 621 $m^2$/g). Thus, surface area could play a major role in the activity of the catalyst in this ultrasound-assisted reaction.

#### *3.2.2. The effect of HPA loading*

The results of catalytic experiments for FAME production yield from Jatropha oil under ultrasonic irradiation for different catalyst loadings are presented in Fig. 4. The reaction yield increased as the TPA content in the catalyst was increased and reached its highest level with TPA20-AC. Meanwhile, the catalyst with higher TPA amount did not show better yield as expected. At low TPA content, the presence of active sites on the surface of the support promoted the conversion of the reactants and drove the system towards forward reaction. Excessive amount of TPA in TPA25-AC led to a slight decrease in the reaction yield mainly due to a reduction in the catalyst surface area accessible by the reactants. This behavior was caused by partial blockage of the pores by the active sites leading to internal diffusion limitation for the reactants. Deposition of TPA particles on the pore mouths could cause the surface area within



(a)

| Element | Wt% | At% |
|---|---|---|
| C K | 100 | 100 |

(b)

| Element | Wt% | At% |
|---|---|---|
| C K | 78.65 | 93.12 |
| O K | 06.44 | 05.72 |
| W M | 14.91 | 01.15 |

(c)

| Element | Wt% | At% |
|---|---|---|
| C K | 71.49 | 92.03 |
| O K | 06.32 | 06.11 |
| W M | 22.19 | 01.87 |

(d)

| Element | Wt% | At% |
|---|---|---|
| C K | 71.49 | 92.03 |
| O K | 06.32 | 06.11 |
| W M | 22.19 | 01.87 |
| P K | 03.51 | 02.07 |

**Fig. 3.** EDAX for the surface of (a) AC (b) TPA15-AC (c) TPA20-AC (d) TPA25-AC.

the pores to be unavailable for the reaction. Low accessibility of the reactants to the active sites in the internal pores resulted in negative effect on the reaction yield. Based on these results, TPA amounts above 20% w/w loading were not recommended due to the decrease in pore volume and surface area due to pore plugging.

In any supported catalyst system, the impregnation of excessive amount of active component will usually lead to loss of surface area and pore volume as observed in this study. As impregnation method was used to prepare the catalyst, the deposition of TPA on the external surface could not be totally avoided. The support material used was also known to contain irregular pore shapes and sizes [15]. As such, it is understandable that if the deposition of the active component occurs at pore mouths, internal diffusion resistance could result. Thus, decreases in these surface properties could affect the catalytic activity in this heterogeneous reaction system. In this respect, SEM images could not clearly show pore mouth blockage as it could also occur at internal narrow areas of the pores.

### 3.2.3. *Effect of reaction time*

Effect of reaction time on the methyl ester yield under ultrasonic condition can be seen in Fig. 5 for both TPA20-AC and TPA25-AC catalysts. For a low reaction time of 20 min, insufficient contact time between the reactants led to low reaction yield. The yield increased with increasing reaction time, reaching its maximum levels in 40 min for both catalysts. The highest reaction yields were 87.33% and 71.19% for TPA20-AC and TPA25-AC, respectively. The behavior of the reaction between 30 and 50 min in the presence of heterogeneous catalyst can be explained based on the role of ultrasonic mixing in achieving emulsifying effects between the reactants. The ultrafine mixing provided a dispersion effect to the catalyst particles through the reaction media that facilitated the reactants molecules to spread and reach the active sites on the surface of the catalyst. The role of ultrasonic irradiation in enhancing the reaction rate for heterogeneous biodiesel production system has been highlighted by Salamatinia et al. [34] and Mootabadi et al. [35]. In these studies, the reaction times to reach yields exceeding 90% in a base-catalyzed transesterification of palm oil

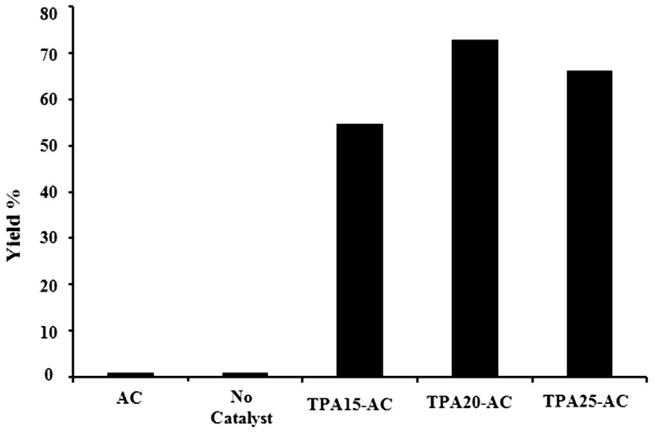


**Fig. 4.** Transesterification of Jatropha oil by ultrasonic-assisted process over TPA immobilized on AC (reaction time 60 min, methanol/oil molar ratio 20:1, catalyst amount 4% (w/w), and ultrasonic power 75%).

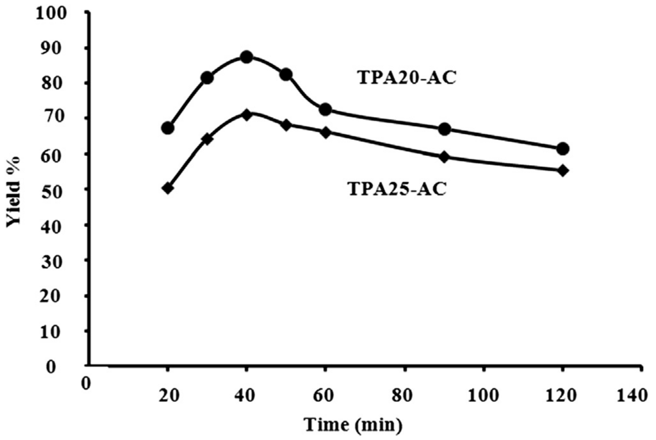


**Fig. 5.** Effect of reaction time on biodiesel yield (methanol/oil molar ratio 20:1, catalyst amount 4% (w/w), and ultrasonic power 75%).

were about ∼50 min and 60 min, respectively. The results were significantly lower than those generally reported for non-ultrasonic reaction systems.

Although the use of ultrasonic irradiation managed to shorten the reaction time, decreases in FAME yields for both catalysts were observed after 60 min. It has been reported for ultrasound-assisted transesterification system that monoglycerides content was high at times beyond 60 min due to the slow reaction rate to convert it to glycerol and FAME [36]. Thus, in the current investigated system, the reaction mixture could contain sufficient amounts of monoglycerides at high reaction time that could enhance the solubility of FAME in the glycerol to result in FAME glycerolysis. Besides that, side (esterification) reactions between FFA and glycerol led to the formation of monoglycerides, diglycerides and finally triglycerides that would negatively affect the reaction yield [15]. Esterification reaction is known to be an acid-catalyzed reaction.

Transesterification process of vegetable oil and methanol is widely reported to be catalyzed by either acid or base catalyst. The reaction rate is influenced by many factors such as the reaction temperature, type of catalyst, ratio of reactants, concentration of the limiting reactant etc. [13,14]. In this study, high concentration of FAME was expected after a certain duration of time, especially when the FAME yield exceeded about 70%. At this stage, FAME glycerolysis could occur at a significantly high rate leading to lower FAME yield. At the same time, the formation of FAME through transesterification between the oil and methanol occurred simultaneously but at low rate due to the low concentration oil as the limiting reactant. As such, with progressing reaction time, more FAME could have been used in the glycerolysis compared to that formed through the transesterification reaction.

Cao et al. [37] reported that by using $H_3PW_{12}O_{40}-6H_2O$ as the catalyst, the highest transesterification yield of 87% could be achieved with high reactants' molar ratio of 70:1 and long reaction time of 14 h under mechanical stirring. On the other hand, with the use of immobilized form of HPA (zirconia-supported HPA catalyst), Sunita et al. [23] recorded that the optimum reaction time under conventional process to achieve 97% of biodiesel yield at 200 °C was 5 h. Thus, the ultrasonic-assisted reactor system significantly reduced the requirement for a very high methanol to oil ratio for the acid catalyzed process. In addition, significant reductions in reaction time and reaction temperature were achieved. Thus, the reaction could be carried out in a more cost efficient manner.

### 3.2.4. Effect of water and FFA content

The effect of feed stock water content on FAME yield for both catalysts can be seen in Fig. 6. It is noted that by increasing the content of water in Jatropha oil to 1% (w $H_2O$/w oil), only a slight decrease in the yields for both catalysts resulted. The results revealed the tolerance of the catalysts towards water. For TPA20-AC, the amount of water beyond 1% led to a sharp decrease in the biodiesel yield while lower yield was recorded for the higher water content (4%). In the case of TPA-25AC catalyst, increasing water content gradually decreased the methyl ester yield. However, water contents beyond 2% did not result in significant decrease in the yield. It could be due to the excess amount of TPA loaded onto the AC.

As a conclusion, a decrease in reaction yield with increasing of water content could be attributed to the hydrolysis of the esters at high water content. The presence of large amount of water could negatively affect the strength of Brönsted acid sites presented in the catalyst. The hydration of these acid sites could reduce the catalyst activity that in turn, resulted in negative effects on the reaction yield. Nakajima et al. [38] reported the same behavior for carbon based acid catalyst used in the presence of high water content. Good tolerance to high water content as demonstrated by TPA25-AC catalyst could be related to the higher number of active sites that reduced the effects of acid sites hydration.

The effect of FFA % content in the crude vegetable oil on the reaction yield is presented in Fig. 7 for TPA20-AC and TPA25-AC catalysts. It can be concluded that both catalysts were insensitive to the presence of FFA. Beyond 17.5 FFA %, slight reductions in the reaction yields for both of catalysts were noticed. This could be attributed to the effect of high amount of water generated during the esterification reaction due to the high FFA content. The presence of water can affect negatively on the production yield as it can hydrolyze the esters. Meanwhile, the studied catalysts showed good water and FFA tolerance which would enable the use of low grade, cheap price and non-edible vegetable oils for biodiesel production.

### 3.2.5. Catalyst reusability and stability

In order to study the catalyst reusability under the ultrasonic conditions, consecutive reaction runs were carried out using the same catalyst. After the first experimental run, the TPA20-AC catalyst was filtered and washed several times with ethanol to remove any polar impurities followed by washing with n-hexane to eliminate any non-polar components. The washed catalyst was dried at 100 °C for 2 h and reused again for the transesterification reaction. Fig. 8 shows the catalyst activity for up to three times of use at 75% of ultrasonic amplitude, 40 min of reaction time and reactants' molar ratio of 20. The results revealed that a drop in the catalytic activity as indicated by a decrement in the reaction yield

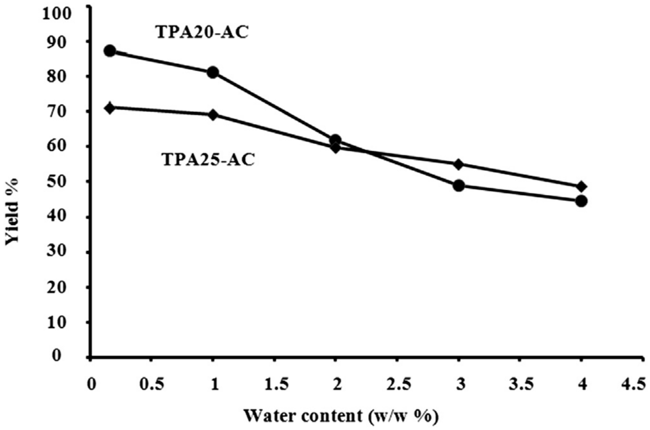


**Fig. 6.** Effect of water content on biodiesel yield (reaction time 40 min, methanol/oil molar ratio 20:1, catalyst amount 4% (w/w), and ultrasonic power 75%).

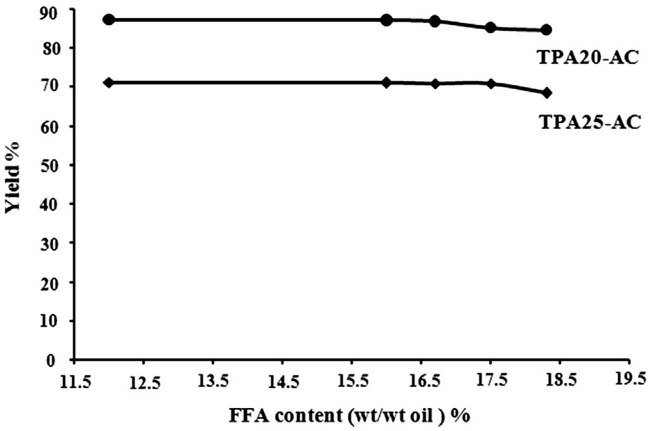


**Fig. 7.** Effect of FFA content on FAME yield (reaction time 40 min, methanol/oil molar ratio 20:1, catalyst amount 4% (w/w), and ultrasonic power 75%).

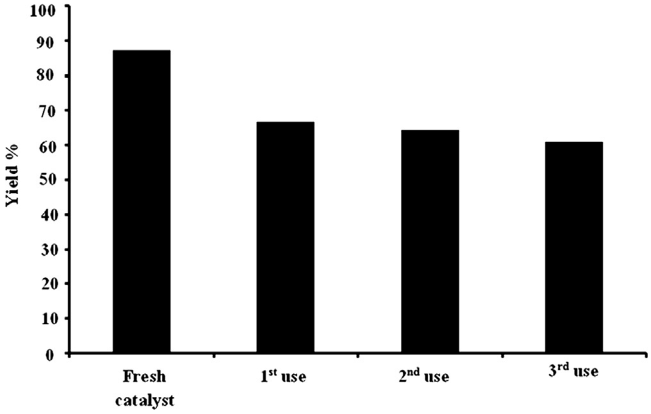


**Fig. 8.** Catalytic activity for successive reaction runs (reaction time 40 min, methanol/oil molar ratio 20:1, catalyst amount 4% (w/w), and ultrasonic power 75%).

was noticed. For the first run, 77% of the original activity was achieved. The reduction in activity could be attributed to the catalyst deactivation, leaching and the loss during washing process between the reuse cycles. A small portion of the solid catalyst was collected as soot in the filtration step during the study. These small carbon particles were formed as a result of the impact of ultrasonic irradiation on the porous solid particles. If the small loss of unrecovered catalyst were to be considered, small drop in the activity from the first run to the third reuse cycle could indicate the stability of the catalyst for repeated use in the process.

The stability of the AC-based TPA catalysts was found to be slightly lower than that reported previously using alumina-based TPA catalysts [33]. For comparison, 20 wt. % TPA loading in AC showed about 27% drop FAME yield after the 3rd cycle of reuse while it was only about 12% in the case of the alumina-based TPA catalyst. Differences in the activity could be associated with the higher structural stability of the alumina-based catalyst. Thus, structural stability could play a major role in the activity of the catalyst in this ultrasound-assisted reaction. Due to higher porosity of AC-based catalyst, its structural stability was expected to be significantly lower compared to that of alumina-based catalyst.

### 3.2.6. *Catalyst leaching*

Investigation on the catalyst stability under the ultrasonic reaction conditions revealed that 12% of the reaction yield was achieved due to the $PW_{12}O_{40}^{3-}$ anion which leached out from the heterogeneous catalyst. The result showed that major part of the reaction yield was achieved through heterogeneous catalysis. Leaching of active sites from the catalyst occurred due to the good solubility of TPA in the polar reaction mixture and the exposure of the solid catalyst to direct ultrasonic irradiation. However, significant solubilization of TPA did not occur as it was strongly fixed on the surface through calcination and the small pore sizes of the AC support.

Compared with other immobilized forms of HPA on different supports such as zirconia and silica [39], HPA supported on AC used in the current study showed minimal leaching due to the strong fixation of HPA over the surface of activated carbon. Some TPA particles were trapped inside the small pores of the support due to textural porous properties of the support material. Strong electrostatic attraction between TPA species and AC could also happen due to the existence of specific functional groups on the surface of AC [39]. The same behavior of HPA immobilized on AC catalyst was reported for other polar reaction mixtures such as acetylation of glycerol with acetic acid [21] and liquid phase esterification of acetic acid with butanol [40].

## 4. Conclusions

Ultrasonic-assisted transesterification of crude Jatropha oil with the presence of activated carbon-supported tungstophosphoric acid (TPA) catalysts was studied. The catalysts were tested to show their activity in FAME production from Jatropha oil with high FFA content using an ultrasound-assisted reactor system. Amount of TPA deposited on the support had significant effects on the catalyst characteristics and subsequently on methyl ester yield in the ultrasound-assisted reaction. TPA20-AC and TPA25-AC catalysts achieved methyl ester yields of up to 87.33% and 71.19%, respectively in just 40 min. Further increase in reaction time beyond 60 min resulted in a reduction in the yield due to the effects of some side reactions. Effect of water and FFA contents in the Jatropha oil on the reaction yield was successfully elucidated. The catalysts showed moderate water tolerance to a limit of 1% w/w water content. The catalysts were also used with high FFA content feed stocks and the results revealed that the catalysts were rather insensitive toward FFA increment in the crude oil. The catalyst reusability and leaching study performed on TPA20-AC catalyst revealed that the reaction was mainly heterogeneous in nature with an appreciable contribution of homogeneous reaction.

## Acknowledgment

A Short Term research grant (60312010) and a Research University grant (814144) from Universiti Sains Malaysia to support this research work are gratefully acknowledged.

## References

[1] Santacesaria E, Di Serio M, Tesser R, Tortorelli M, Turco R, Russo V. A simple device to test biodiesel process intensification. Chem Eng Proc 2011;50:1085–94.
[2] Qiu Z, Zhao L, Weatherley L. Process intensification technologies in continuous biodiesel production. Chem Eng Proc 2010;49:323–30.
[3] Ma F, Hanna MA. Biodiesel production: a review. Bioresour Technol 1999;70:1–15.
[4] Koh MY, Ghazi TIM. A review of biodiesel production from Jatropha curcas L. oil. Renew Sust Energ Rev 2011;15:2240–51.
[5] Leung DYC, Wu X, Leung MKH. A review on biodiesel production using catalyzed transesterification. Appl Energ 2010;87:1083–95.
[6] Boey PL, Ganesan S, Maniam GP, Khairuddean M, Lim SL. A new catalyst system in transesterification of palm olein: tolerance of water and free fatty acids. Energ Convers Manag 2012;56:46–52.
[7] Elsheikh YA, Man Z, Bustam MA, Yusup S, Wilfred CD. Brønsted imidazolium ionic liquids: synthesis and comparison of their catalytic activities as pre-catalyst for biodiesel production through two stage process. Energ Convers Manag 2011;52:804–9.
[8] Math MC, Kumar SP, Chetty SV. Technologies for biodiesel production from used cooking oil – a review. Energ Sust Dev 2010;14:339–45.
[9] Jacobson K, Gopinath R, Meher LC, Dalai AK. Solid acid catalyzed biodiesel production from waste cooking oil. Appl Catal B 2008;85:86–91.
[10] Semwal S, Arora AK, Badoni RP, Tuli DK. Biodiesel production using heterogeneous catalysts. Bioresour Technol 2011;102:2151–61.
[11] Vyas AP, Verma JL, Subrahmanyam N. A review on FAME production processes. Fuel 2010;89:1–9.
[12] Kulkarni MG, Dalai AK. Waste cooking oil – an economical source for biodiesel: a review. Ind Eng Chem Res 2006;45:2901–13.
[13] Jitputti J, Kitiyanan B, Rangsunvigit P, Bunyakiat K, Attanatho L, Jenvanitpanjakul P. Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. Chem Eng J 2006;116:61–6.
[14] Melero JA, Bautista LF, Morales G, Iglesias J, Sánchez-Vázquez R. Biodiesel production from crude palm oil using sulfonic acid-modified mesostructured catalysts. Chem Eng J 2010;161:323–31.
[15] Shu Q, Nawaz Z, Gao J, Liao Y, Zhang Q, Wang D, et al. Synthesis of biodiesel from a model waste oil feedstock using a carbon-based solid acid catalyst: reaction and separation. Bioresour Technol 2010;101:5374–84.
[16] Morin P, Hamad B, Sapaly G, Carneiro-Rocha MG, de Oliveira PGP, Gonzalez WA, et al. Transesterification of rapeseed oil with ethanol: I. Catalysis with homogeneous Keggin heteropolyacids. Appl Catal A 2007;330:69–76.
[17] Chai F, Cao F, Zhai F, Chen Y, Wang X, Su Z. Transesterification of vegetable oil to biodiesel using a heteropolyacid solid catalyst. Adv Synth Catal 2007;349:1057–65.

[18] Zhang S, Zu YG, Fu YJ, Luo M, Zhang DY, Efferth T. Rapid microwave-assisted transesterification of yellow horn oil to biodiesel using a heteropolyacid solid catalyst. Bioresour Technol 2010;101:931–6.

[19] Tropecêlo AI, Casimiro MH, Fonseca IM, Ramos AM, Vital J, Castanheiro JE. Esterification of free fatty acids to biodiesel over heteropolyacids immobilized on mesoporous silica. Appl Catal A 2010;390:183–9.

[20] Mukai SR, Lin L, Masuda T, Hashimoto K. Key factors for the encapsulation of Keggin-type heteropoly acids in the supercages of Y-type zeolite. Chem Eng Sci 2001;56:799–804.

[21] Ferreira P, Fonseca IM, Ramos AM, Vital J, Castanheiro JE. Acetylation of glycerol over heteropolyacids supported on activated carbon. Catal Commun 2011;12:573–6.

[22] Katada N, Hatanaka T, Ota M, Yamada K, Okumura K, Niwa M. Biodiesel production using heteropoly acid-derived solid acid catalyst $H_4PNbW_{11}O_{40}/WO_3\text{-}Nb_2O_5$. Appl Catal A 2009;363:164–8.

[23] Sunita G, Devassy BM, Vinu A, Sawant DP, Balasubramanian VV, Halligudi SB. Synthesis of biodiesel over zirconia-supported isopoly and heteropoly tungstate catalysts. Catal Commun 2008;9:696–702.

[24] Badday AS, Abdullah AZ, Lee KT, Khayoon MS. Intensification of biodiesel production via ultrasonic-assisted process: a critical review on fundamentals and recent development. Renew Sust Energ Rev 2012;16:4574–87.

[25] Gogate PR. Cavitational reactors for process intensification of chemical processing applications: a critical review. Chem Eng Proc 2008;47:515–27.

[26] Ji J, Wang J, Li Y, Yu Y, Xu Z. Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation. Ultrasonics 2006;44:e411–4.

[27] Deng X, Fang Z, Liu YH. Ultrasonic transesterification of Jatropha curcas L. oil to biodiesel by a two-step process. Energ Convers Manag 2010;51:2802–7.

[28] Hanh HD, Dong NT, Starvarache C, Okitsu K, Maeda Y, Nishimura R. Methanolysis of triolein by low frequency ultrasonic irradiation. Energ Convers Manag 2008;49:276–80.

[29] Chimienti ME, Pizzio LR, Cáceres CV, Blanco MN. Tungstophosphoric and tungstosilicic acids on carbon as acidic catalysts. Appl Catal A 2001;208:7–19.

[30] Obali Z, Doğu T. Activated carbon–tungstophosphoric acid catalysts for the synthesis of tert-amyl ethyl ether (TAEE). Chem Eng J 2008;138:548–55.

[31] Alemdaroglu T. Determination methods for the acidity of solid surfaces. Commun Fac Sci Univ Ank Ser B 2001;47:27–35.

[32] Taufiq-Yap YH, Lee HV, Yunus R, Juan JC. Transesterification of non-edible Jatropha curcas oil to biodiesel using binary Ca–Mg mixed oxide catalyst: effect of stoichiometric composition. Chem Eng J 2011;178:342–7.

[33] Badday AS, Abdullah AZ, Lee KT. Ultrasound-assisted transesterification of crude Jatropha oil using alumina-supported heteropolyacid catalyst. Appl Energ 2013;105:380–8.

[34] Salamatinia B, Mootabadi H, Bhatia S, Abdullah AZ. Optimization of ultrasonic-assisted heterogeneous biodiesel production from palm oil: a response surface methodology approach. Fuel Proc Technol 2011;91:441–8.

[35] Mootabadi H, Salamatinia B, Bhatia S, Abdullah AZ. Ultrasonic-assisted biodiesel production process from palm oil using alkaline earth metal oxides as the heterogeneous catalysts. Fuel 2010;89:1818–25.

[36] Stavarache C, Vinatoru M, Maeda Y. Aspects of ultrasonically assisted transesterification of various vegetable oils with methanol. Ultrason Sonochem 2007;14:380–6.

[37] Cao F, Chen Y, Zhai F, Li J, Wang J, Wang X, et al. Biodiesel production from high acid value waste frying oil catalyzed by superacid heteropolyacid. Biotechnol Bioeng 2008;101:93–100.

[38] Nakajima K, Hara M, Hayashi S. Environmentally benign production of chemicals and energy using a carbon-based strong solid acid. J Am Ceram Soc 2007;90:3725–34.

[39] Sepúlveda JH, Yori JC, Vera CR. Repeated use of supported $H_3PW_{12}O_{40}$ catalysts in the liquid phase esterification of acetic acid with butanol. Appl Catal A 2005;288:18–24.

[40] Alsalme A, Kozhevnikova EF, Kozhevnikov IV. Heteropoly acids as catalysts for liquid-phase esterification and transesterification. Appl Catal A 2008;349:170–6.